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minerals from Cobalt

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# A STUDY OF CERTAIN MINERALS

FROM

# COBALT, ONTARIO

By  
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*incident*  
H. V. ELLSWORTH

A Thesis submitted in conformity with the requirements  
for the Degree of Doctor of Philosophy in the  
University of Toronto.

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Reprinted from Vol. XXV., Part I,  
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# A STUDY OF CERTAIN MINERALS FROM COBALT, ONTARIO

By  
H. V. ELLSWORTH

In presenting this paper on certain mineral associations of Cobalt, the writer believes that, considering the importance of this famous mining region, no apology is necessary for the somewhat detailed descriptions in which he has been tempted to indulge.

The geology of the Cobalt area has received a great deal of attention, naturally, and has been admirably described by W. G. Miller and his associates in the reports of the Ontario Bureau of Mines. To them also is to be credited most of the published mineralogical data relating to Cobalt. In the Nineteenth Report of the Ontario Bureau of Mines, Part II, was included a descriptive list of the minerals which were known from Cobalt at that time, together with remarks on their mode of occurrence, and a table in which the probable order of deposition of the chief minerals was indicated. The order of deposition was also worked out by Campbell and Knight<sup>1</sup> from observations on polished surfaces by the metallographic method.

Early in 1914, at the suggestion of T. L. Walker, Professor of Mineralogy at the University of Toronto, the writer undertook an investigation of breithauptite ore from the Hudson Bay mine. The results of this investigation seemed to have a bearing on the question of isomorphous inter-growths and led to a study of other mineral associations from Cobalt. Dr. Walker very kindly allowed the writer the use of the numerous specimens from Cobalt in the collection of the Royal Ontario Museum of Mineralogy, and in this way the work gradually broadened in scope.

In the following pages no attempt has been made to deal exhaustively with all the common minerals of Cobalt. Only such associations have been studied as were interesting because of the minerals hitherto unidentified from Cobalt, because of rarity or unusual crystallization, or because of a possible bearing on questions of isomorphism or paragenesis. These investigations have added the following to the list of minerals from Cobalt: Löllingite, rammelsbergite, chalcocite and symplectite.<sup>2</sup>

The objects of the investigation may thus be summarized as follows:

1. Descriptive: Identification and crystallographic study of special minerals, rare, or new to Cobalt. Identification in the case of the complex ores of Cobalt usually involves—2.

2. (a) Chemical analysis and separation experiments.

(b) Microscopic study of polished surfaces.

3. Study of structures having a bearing on isomorphism.

4. Order of deposition or paragenesis, as shown by study of microscopic structures.

<sup>1</sup> Microscopic examination of the Cobalt-Nickel Arsenides and Silver Deposits of Temiskaming by W. Campbell and C. W. Knight, *Ec. Geol.*, Sept.-Oct., 1906.

<sup>2</sup> The Paragenesis of the Cobalt-Nickel Arsenides and Silver Deposits of Temiskaming, *Eng. and Min. Jr.*, June 9th, 1906.

<sup>3</sup> For list of Cobalt minerals see *Report Ont. Bur. Mines*, Vol. XIX, Pt. II, p. 9.

### Methods of Microscopic Examination and Separation

The preparation of polished sections of minerals for examination by the metallographic method has been treated in detail by Campbell and Knight.<sup>4</sup>

The use of acids or other corrosive re-agents for developing the structure of polished surfaces of metals or minerals probably originated in the study of meteoric iron, the so-called Widmanstätten figures having been described in 1808. Outside of its application to meteoric iron, but little use seems to have been made of this method in mineralogy until Baumhauer<sup>5</sup> in 1886, applied it to the study of crystals of smaltite-chloanthite, with extremely interesting results. Vollhardt<sup>6</sup> analyzed the crystals which had been examined by Baumhauer before and after treatment with hydrochloric acid and potassium chlorate, and found that the residue left after the acid treatment was considerably richer in arsenic than the original material. From this result he deduced the presence of skutterudite ( $\text{CoAs}_3$ ) in the smaltite-chloanthite crystals.

The writer has applied similar methods to the study of microscopic intergrowths from Cobalt. If a polished surface of a complex ore, containing two or more minerals closely intergrown, say smaltite and chloanthite, which are quite indistinguishable by ordinary means, be slightly etched with acid, the two minerals become easily distinguishable owing to the different effect of the acid upon them. If the etching be continued for a longer time one mineral will finally be corroded much deeper than the other, which stands in relief. It occurred to the writer that this method might be used to liberate minerals from the minute inclusions which are so characteristic of minerals from Cobalt, and it has, in fact, been used with success in some instances (see Breithauptite, page 13).

This difference in the action of an acid on the two minerals is not due entirely to the difference in the rate of solution of the individual minerals taken separately in acid of a given concentration. Gottschalk and Buehler<sup>7</sup> have shown that there is a difference of potential between different natural minerals and that two minerals in contact act as a battery in oxidation experiments, the current flowing from the mineral of higher potential, which is protected from the action of the oxidizing agent, while the mineral of lower potential dissolves more rapidly. There are also of course, instances in which one of the minerals reacts with the acid to form an insoluble coating which protects it while the other mineral is being dissolved away. Such coatings on a mineral of lower potential may, in certain instances, cause a reversal of the normal action, so that the mineral of higher potential actually dissolves more rapidly.<sup>8</sup>

Palmer and Bastin<sup>9</sup> have recently advocated the use of silver sulphate solution to separate arsenides from sulpharsenides and sulphides, the sulphate being chosen because of the bearing of their experiments on silver enrichment. The writer has

<sup>4</sup> Loc. cit.

<sup>5</sup> Ueber die Structur und die mikroskopische Beschaffenheit von Speiskobalt und Chloanthit, von H. Baumhauer, *Zeitschrift für Krystallographie* 12, 18, 1887.

<sup>6</sup> Versuche über Speiskobalt—von G. Vollhardt, *Zeitschrift für Krystallographie* 14, 407, 1888.

<sup>7</sup> Oxidation of Sulphides—V. H. Gottschalk and H. A. Buehler—*Ec. Geol.*, Vol. VII, No. 1, Jan., 1912.

<sup>8</sup> Breithauptite, page 13.

<sup>9</sup> Tetranickel Triarsenide, Its Capacity as a Silver Precipitant, Chase Palmer, *Econ. Geol.*, Vol. IX, No. 7, Oct., 1914.



used silver nitrate solution with equal success, and this has the advantage that it can be made up in much stronger solutions than the sulphate, which is not very soluble. With the nitrate solution results are obtained in less time and with much smaller volumes of solutions.

It should be remembered, however, that all the foregoing methods are capable under favourable conditions of producing only a pure residue. The less soluble mineral is not entirely unaffected by acids or silver solutions and will also enter into solution to a certain extent, so that the resultant solution contains the constituents of both minerals. The residue, after sufficiently long action should, theoretically, be pure.

### Methods of Chemical Analysis

In general, the writer has used the methods recommended by Treadwell, 1914 edition. As different methods do not always yield identical results, those used here may be summarized as below:

*Arsenic*—Usually determined by the Pearce method.<sup>10</sup> After fusion of the ore with a mixture of sodium carbonate and nitrate, the alkali arsenate is leached out and converted into silver arsenate which is titrated with ammonium sulphocyanate solution. If the solution to be titrated contains the same amount of silver as was used for standardizing the sulphocyanate solution, the results are very accurate.

*Antimony*—Weighed as  $Sb_2S_3$  after heating in a current of carbon dioxide.

*Bismuth*—Weighed as sulphide or oxide. Separated from lead by basic nitrate method.

*Copper*—By electrolysis of sulphuric acid solution.

*Iron*—Separated from nickel and cobalt by one or more precipitations as basic acetate followed by precipitation as hydroxide from nitric acid solution and weighing as  $Fe_2O_3$ . The writer has found that if the hydroxide be precipitated along with finely macerated ashless filter paper as recommended by Washington,<sup>11</sup> there is no danger of the formation of magnetite on ignition and the results agree exactly with permanganate titrations.

*Lead*—Weighed as sulphate in Gooch crucible.

*Mercury*—Weighed as sulphide after reprecipitation.

*Nickel and Cobalt*—Determined together by electrolysis of ammonium sulphate solution, using a revolving cathode. Nickel separated and weighed as nickeldimethylglyoxime, cobalt by difference. In precipitating small amounts of nickel from large quantities of cobalt, a very large excess of the rather expensive dimethylglyoxime is required, in fact more than enough to combine with all the cobalt must be used in order to precipitate all the nickel. In such cases, the writer first precipitates the cobalt as tripotassium cobaltic nitrite, the nickel in the acetic acid filtrate is then readily precipitated by a relatively small amount of dimethylglyoxime.

*Silver*—As chloride.

*Sulphur*—Usually by fusion of the ore with alkali carbonate and nitrate, or with a mixture of sodium carbonate and sodium peroxide. Weighed as barium sulphate. The writer has not obtained quite as concordant results with the sodium

<sup>10</sup> Low—Technical Methods of Ore Analysis.

<sup>11</sup> The Chemical Analysis of Rocks—H. S. Washington.

peroxide method as with the old Fresenius method. All analyses, except where otherwise noted, have been made in duplicate.

### Native Silver

The silver of Cobalt, as is well known, usually contains both antimony and mercury. It has been generally supposed that the mercury is alloyed with the silver as amalgam, and that the antimony is in the form of dyscrasite.

It was thought that a microscopic examination of analyzed specimens might throw some light on the manner in which the antimony is combined with the silver.

Five specimens were analyzed as below:

	Ag	Sb	Hg	S	Co or Ni	As	Insol.	Total
I	93.61	5.89	.35	trace	trace	....	....	99.85
II	95.39	3.31	trace	.63	trace	....	.60	99.93
III	99.56	.17	trace	trace	....	trace	....	99.73
IV	92.60	6.59	.34	trace	trace	....	.22	99.75
V	90.54	.79	3.08	trace	trace	....	5.50	99.91

I. Slab silver— $\frac{1}{8}$  to  $\frac{1}{4}$  inch thick, Buffalo mine.

II. do do do Cobalt.

III. Thin leaf silver, Nova Scotia mine.

IV. Brittle moss-like silver, Cobalt.

V. Thin leaf silver from oxidized arsenate ore—Penn-Canadian mine. The 5.50 per cent. insoluble represents, chiefly, flakes of argentite which was separated approximately by using cold dilute nitric acid to dissolve the silver.

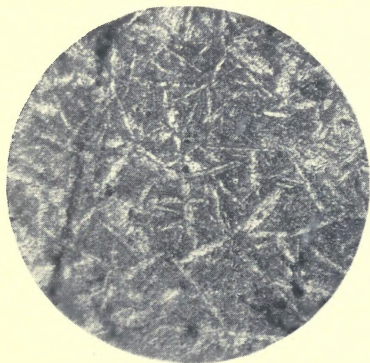


Fig. 1. Skeleton crystals of dyscrasite (?) in native silver, x 50.

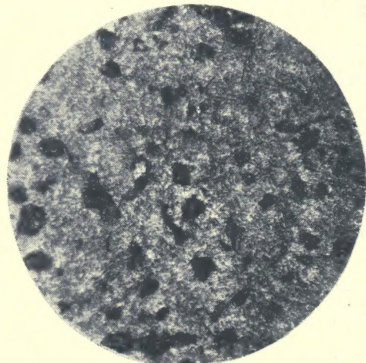


Fig. 2. Inclusions of argentite in native silver, x 50.

There is not enough antimony in any of these samples to form dyscrasite of theoretical composition and the question arises, does antimony combine chemically with silver in various proportions or is dyscrasite of theoretical composition alloyed or mixed with the silver. The stellate structure (Fig. 1) developed by etching a

surface of silver, specimen No. 1, would furnish a partial answer to this question if we admit that these radiating structures represent skeleton crystals of dyscrasite set in a ground-mass of silver, as seems probable from the antimony content of this sample (5.89 per cent. Sb.)

The specimen of silver, No. III, contained but very little antimony and mercury and developed no noteworthy structure on etching, only a few small inclusions being noted. The homogeneous character of the etched surface agrees with its chemical purity.

In the preparation of the samples special care was taken to exclude all visible foreign adhering material. In spite of this all showed traces of sulphur and one, No. II, showed a notable quantity. The sulphur appears to be due to the presence of argentite as minute inclusions in the silver. Microscopic examination of a sur-

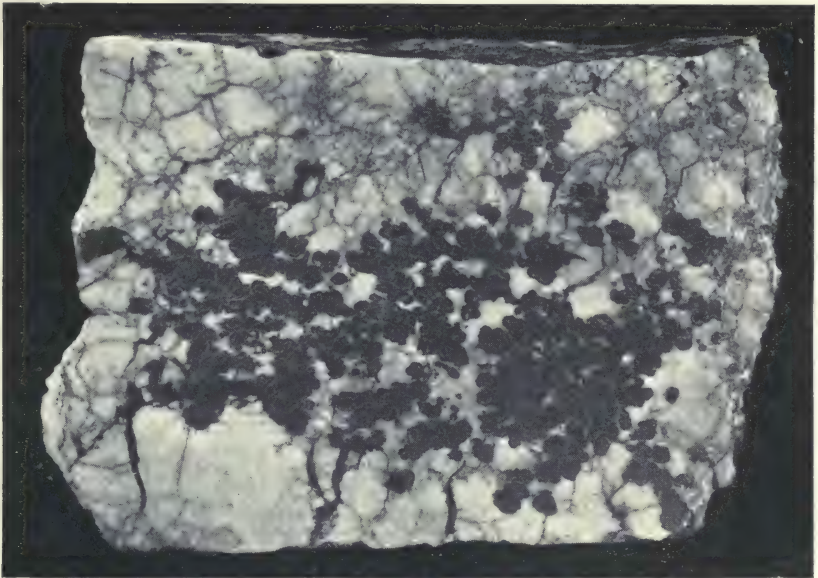


Fig. 2. Cross-section (natural size) of a rich silver vein, showing silver replacing arsenides and calcite.

face of No. II etched by nitric acid shows inclusions of a gray mineral which stands in relief and, therefore, must resist the acid better than silver (Fig. 2). This behaviour agrees with the known resistant character of argentite to cold dilute nitric acid.

There appears to be no relationship between the amounts of antimony and mercury in these analyses, but there can be no doubt whatever that the mercury is alloyed with the silver. Analyses of mineral samples in which silver is absent never show any trace of mercury and in this the writer's experience agrees with that of G. H. Clevenger of the Nipissing mill. Mr. Clevenger also shows that in the Cobalt ores he has analyzed the amount of mercury found is proportional to the silver content.<sup>12</sup>

<sup>12</sup> Note upon The Occurrence of Mercury on Cobalt Ores, by G. H. Clevenger, Econ. Geol., Vol. X, No. 8, December, 1915.

*Paragenesis:* Close examination of silver from Cobalt, in the writer's experience, always reveals the presence of more or less argentite, usually as thin amorphous coatings or scales attached to the surface of the silver. Thin coatings or patches of ruby silver are also common. Sometimes veinlets of argentite have a thin film of silver next the vein walls (Fig. 4). That the association of silver and argentite is very intimate is further shown by the presence of minute argentite inclusions in massive leaf silver (Fig. 2), as well as by the detection of traces of sulphur in several other samples. It is difficult to decide whether such structures are due to replacement or to more or less contemporaneous precipitation of both argentite and silver. At any rate the silver and argentite are later than the arsenide-sulpharsenide minerals since veinlets of silver may be seen cutting the latter (Fig. 3). Most of the silver fills in cleavage cracks and fractures or replaces calcite or arsenides. Fig. 3, a cross section of a typical very rich silver vein, illustrates well the replacement of arsenides by silver. In the picture both silver and

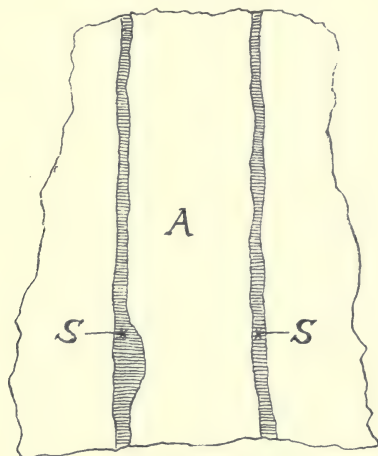


Fig. 4. Veinlet of argentite (*A*) with fibrous native silver (*S*) at the sides. The veinlet is about 2 mm. in width.

smaltite are dark, but the smaltite being harder has resisted buffing better and stands in relief. In the lower part of the picture native silver has almost completely replaced the arsenides, of which only a few fragments remain. In the upper part, the silver for the most part occupies the centre of the dendritic arsenide growths, and in some places can be seen connecting with veinlets in the calcite. There can be little doubt that in this case the arsenide minerals have been chiefly responsible for the precipitation of silver, and apparently the mineral which was originally in the centre of the dendritic growths was much more effective than the part that remains. This sort of structure might be expected to result from the reaction of cobalt-nickel arsenides on silver sulphate solution which has been demonstrated experimentally by Palmer and Bastin.<sup>13</sup> The writer's conception of the probable process is as follows:—The solutions from which the Cobalt ores were precipitated were at first very rich in arsenic, resulting in the precipitation of diarsenides, followed by arsenides. The arsenic content of the mother solution decreased as sul-

<sup>13</sup> Loc. cit.

phur became more prominent and sulpharsenides were also deposited. Finally the arsenic was practically all precipitated and the solution was essentially of a sulphate character. About this time came a slight movement, resulting in fracturing. The sulphate solution now carrying chiefly silver had an excellent opportunity to penetrate the fractured veins and come in contact with the arsenides which were dissolved while metallic silver and argentite were precipitated, resulting in replacement structures such as we have seen. No doubt the calcite also was concerned in the precipitation to an important degree. The dissolved arsenides were ultimately deposited elsewhere, resulting in structures in which the normal order of precipitation might appear to be reversed. Certain structures, the interpretation of which is very doubtful, do occur. Fig. 5 shows a beautiful dendritic growth of smaltite, with a very little niccolite, that is very suggestive of the tree-like crystallizations of silver. A few of these little tubes of smaltite are filled with silver, but calcite occupies the centre of most of them. There are also a few minute veinlets of native silver in the calcite.

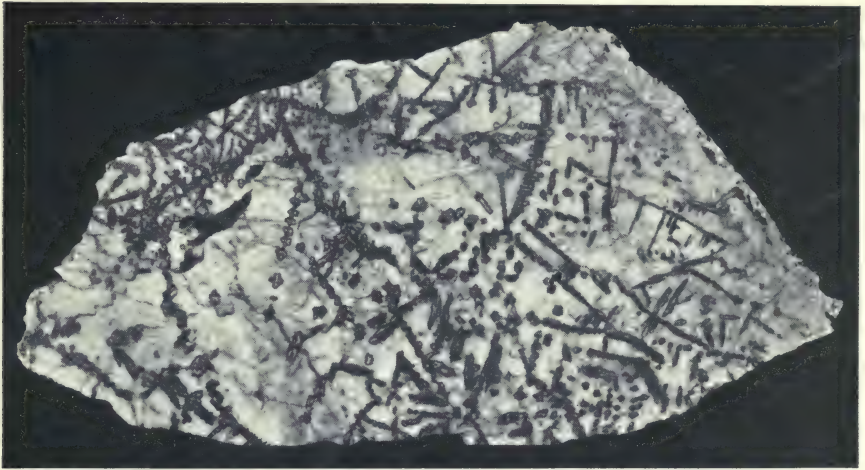


Fig. 5. Dendritic growths of smaltite, with native silver in calcite, reduced to three-quarters natural size.

#### Argentite Crystals, Casey-Cobalt Mine

A specimen from the Casey-Cobalt mine showed crystallized surfaces of argentite embedded in pure cleavable calcite. The argentite is closely associated with partially crystallized pyrite and these two minerals appear to have replaced or impregnated typical massive smaltite ore which makes up the rest of the specimen. In places, the argentite is intergrown with delicate filmy forms of native silver. On dissolving away the calcite with hydrochloric acid several well-developed, lustrous crystals of argentite were revealed. Examination of these crystals indicates that they occur in two distinct habits: 1. Simple, half-octahedrons attached vertically to the argentite mass, the plane of attachment corresponding to the direction of a cube face, and 2. Somewhat tabular forms which proved to be combinations of the rhombic dodecahedron, cube, tetrahedron, trisoctahedron and tetrahexahedron (Fig. 6). These are also attached in a plane parallel to a cube face. A

single crystal of the latter type about 1 x 1.5 x 1.5 mm. in size was found to have good faces suitable for measuring. Using the two-circle goniometer good signals were obtained for most of the faces, the only ones which are at all doubtful being the two faces belonging to the tetrahexahedron (510). These faces are small and the signals are faint and hazy. They are certainly in a zone with cube and dodecahedral faces. The best readings on the horizontal circle gave values for  $\rho$  of  $77^{\circ} 50'$  and  $79^{\circ} 10'$  for the two faces. These faces have been interpreted as belonging to the form (510) of the tetrahexahedron, a form which has not been recorded by Goldschmidt or Hintze as having been hitherto observed on argentite but which does occur on fluorite.<sup>11</sup> The theoretical value of  $\rho$  for (510) is  $78^{\circ} 41'$ . Faces belonging to the following forms have been observed on the crystal: c (100); d (110); q (211); u (221); and  $\epsilon$  (510).

The drawing (Fig. 6) is intended to represent this crystal in its natural proportions, and shows only the faces actually present.

This is probably the first measurable crystallized argentite recorded from Canada.

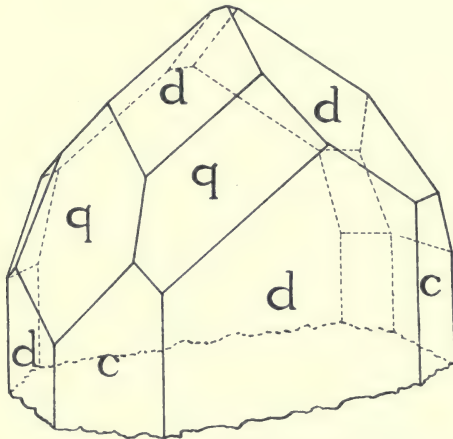


Fig. 6. Argentite, Casey-Cobalt mine.

Some of the partially crystallized argentite of this specimen was analyzed with the following results:

	Ag	S	Fe	Quartz	Sb (?)	Total
Per cent.	86.80	13.01	.08	.16	trace	100.05
Mol. Ratio	.8044	.4057	.0014	....	....	....
Argentite Ag <sub>2</sub> S	.8044	.4029	....	....	....	....
Pvrite FeS <sub>2</sub>	....	.0028	.0014	....	....	....

<sup>11</sup> Krystallographische Winkeltabellen—von. V. Goldschmidt.

The argentite is evidently very pure, the pyrite and quartz being merely accidental impurities.

A qualitative test of the pyrite shows that it also is practically pure if care be taken to obtain a sample free from adhering material.

One would be inclined to suspect from all the evidence that these two minerals were formed at a later period than the intimately mixed arsenide vein ore.

### Argentite, O'Brien Mine

A specimen of argentite from the O'Brien mine attracted attention because of its peculiar iridescent tarnish resembling that of bornite, or perhaps more like the many-coloured tarnish which silver dishes assume after standing idle for some time in the laboratory. It was thought that this tarnish might indicate some variation in composition, and the mineral was accordingly analyzed. It proved to be ordinary argentite.

Ag	S	Sb or As	Cu	Co	Insol.	Total
86.91	12.86	trace	trace	trace	trace	99.77

This was the specimen from which crystals of polybasite were obtained. In a few places this argentite shows some evidence of a tendency to crystallize in forms which suggest rhombic rather than cubic symmetry. The argentite is associated with typical massive gray arsenide ore.

### Galena Crystals, O'Brien Mine

Several large crystals of galena from the O'Brien mine are in the museum<sup>14a</sup> collection. They are rather remarkable because of their large size (up to 2.5 inches diameter), and because they are essentially octahedral in habit, cube faces when present being only slightly developed. The crystals are rough and have been more or less broken. Small grains and films of quartz can be seen along some of the broken cleavage surfaces, showing the same intimate association with quartz as was observed in the case of the very pure chalcocite from the Foster mine described on page 12.

Analysis of 1 gram samples failed to detect the presence of any impurity, except a small amount of iron.

	Per cent.
Pb .....	86.56 ÷ 207.10 = .4182
Fe .....	.05 ÷ 55.84 = .0009
S .....	13.45 ÷ 32.07 = .4195
<b>Total .....</b>	<b>100.06</b>

The purity of this galena is remarkable when one remembers the usual complex character of Cobalt ores. It is not unlikely that several of the very pure minerals which have been encountered, such as galena, chalcocite, argentite, pyrite and chalcopyrite, which are usually associated with quartz and very pure calcite, belong to a later period of formation than the typical complex vein ores and may have been formed by solution and reprecipitation after the main period of mineralizing activity was finished.

<sup>14a</sup> Royal Ontario Museum, Toronto.

### Chalcocite, Foster Mine

The specimen consists chiefly of white calcite through which runs a veinlet of white granular quartz. The chalcocite occurs as small patches, usually not over a quarter of an inch in diameter, very intimately associated with the quartz, which is later than the calcite.

Analyses of half gram samples showed no impurities except minute quartz grains, as below:

	Actual	Theoretical
Cu .....	79.58 per cent.	79.84 per cent.
S .....	20.10 " "	20.16 " "
Quartz .....	.34	
	<hr/> 100.02	<hr/> 100.00

The mineral is included here because it has not previously been reported from Cobalt, and further because of its unusual purity and freedom from intergrowths of other minerals.

Chalcocite in a disseminated condition may possibly be a constituent of certain of the complex ores which carry copper, but tetrahedrite and chalcopyrite appear to be much more common.

The character of the gangue is noteworthy, the calcite being a white, very cleavable variety encountered before in examining crystallized argentite specimens, and which seems to be quite different from the ordinary vein calcite, which is usually hard and dolomitic. This calcite is very easily soluble and is practically pure calcium carbonate. Minerals with which it is associated are more apt to be crystallized or unusually pure. It probably belongs to a late stage of deposition or it may be of a secondary character.

### Breithauptite Association, Hudson Bay Mine

Within recent years the rather rare mineral breithauptite has been found in the silver-bearing veins of several of the Cobalt mines. Some time ago the Department of Mineralogy, University of Toronto, purchased from the Hudson Bay Mines, Ltd., a quantity of vein material in which this mineral appeared to be prominent. Since no analysis of breithauptite from this locality has been published up to the present, the writer, at the suggestion of T. L. Walker, undertook an investigation of the above material.

The constituent minerals, as will be seen later, proved to be breithauptite, niccolite, cobaltite and native silver, with calcite as the gangue material. In a typical polished hand-specimen, the purplish copper-coloured breithauptite is seen as rounded arborescent patches varying usually from one eighth to one inch along the greatest diameter. These breithauptite areas are always completely enclosed by a relatively narrow band of pale, copper-coloured niccolite, which in turn is fringed by an equally narrow border of gray cobaltite. The layer of cobaltite is sometimes so thin as to be almost indistinguishable to the naked eye. The intervening spaces are filled with white calcite. Finally, in some of the specimens, veinlets of native silver penetrate all the minerals previously mentioned.



### Etching Methods for Breithauptite

In order to study in more detail the structure of breithauptite and other associated minerals, and their relation to each other, various etching re-agents were applied to polished surfaces, with the following results:

I. Strong nitric acid momentarily applied produces a very beautiful effect by darkening the breithauptite while leaving the niccolite bright and unaffected. The cobaltite shows up with a brightness intermediate between breithauptite and niccolite. With a somewhat longer application the breithauptite is strongly attacked with the formation of a white coating of the oxides of antimony. The niccolite is relatively little attacked and if the coating of oxides be removed from the breithauptite, it seems to stand in higher relief than the latter. If, however, the action is allowed to continue until a thick coating of oxides forms on the breithauptite, a point is reached when the niccolite begins to be rapidly dissolved and finally is etched deeper than the breithauptite.

It appears that in the latter case the oxides of antimony form a coating over the breithauptite which tends to protect the mineral beneath from the action of the acid, but since no coating forms on the niccolite it continues to dissolve and finally is etched deeper than the breithauptite.

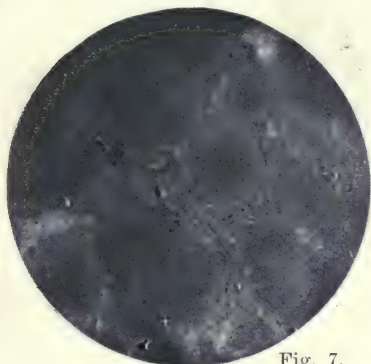


Fig. 7.

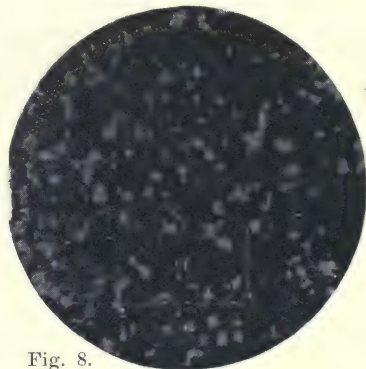


Fig. 8.

Fig. 7. The general structure of breithauptite as seen on a polished surface slightly etched with nitric acid. Magnification about  $1\frac{1}{2}$  diameters.

Fig. 8. Niccolite inclusions in bright relief in a ground mass of dark breithauptite. The darkest spots represent minute cavities in the breithauptite. (x 50).

The addition of tartaric acid to the nitric acid appears to prolong somewhat the time during which breithauptite is attacked with greater rapidity than niccolite. By repeatedly removing the specimen from the acid as soon as a moderately thick coating of oxides has formed and freeing the breithauptite surface of oxide by brushing and treatment with hydrofluoric acid, the breithauptite may be removed, without much affecting the niccolite. This observation suggested a method which is described later of removing breithauptite inclusions from niccolite.

II. Aqua regia attacks strongly both breithauptite and niccolite which dissolves to a clear solution. The cobaltite appears to be scarcely acted upon so long as the other minerals are present and hence stands in the highest relief after etching. By continuing this etching process until the breithauptite and niccolite have been entirely dissolved away, the cobaltite can thus be obtained as a residue free from both breithauptite and niccolite.

III. Hot dilute nitric acid (1-4) dissolves away the niccolite leaving breithauptite standing in relief and practically unaltered. The cobaltite is not perceptibly attacked but crumbles away as the supporting niccolite is dissolved and collects as a residue along with some breithauptite powder at the bottom of the dish. Since, as will be seen later, there are no cobaltite inclusions in the breithauptite itself we can thus eliminate both niccolite and cobaltite from the breithauptite.

Various other re-agents gave negative results or were so slow in action as to be valueless. Hydrochloric and sulphuric acids, strong or dilute, hot or cold, have but little effect. Hydrofluoric acid, though useless as an etching re-agent, proved useful in clearing away the oxides from etched surfaces.

#### Microstructure and Order of Deposition of the Breithauptite and Associated Minerals

The use of the etching methods outlined above produced surfaces in which the individual minerals by their differences in colour and relief could be very easily and clearly distinguished under the microscope or even with a hand lens.

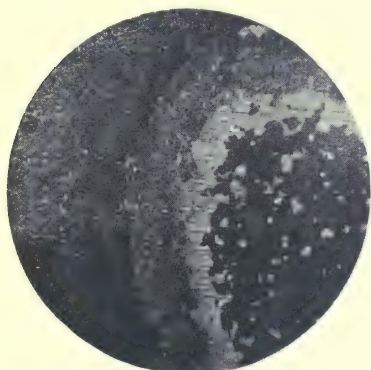


Fig. 9.

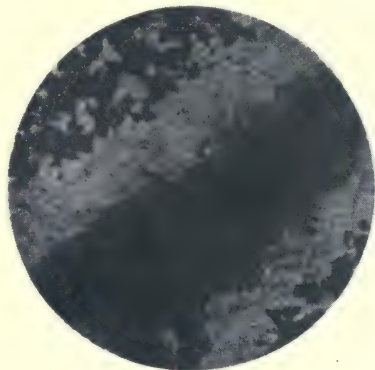


Fig. 10.

Fig. 9. The end of an arborescent area of breithauptite with characteristic niccolite inclusions is seen surrounded by a bright band of niccolite which on its outer edge is fringed by light gray cobaltite. Outside the cobaltite is a black band where calcite has been deeply etched, with two included dark gray areas at the top and bottom which represent calcite or perhaps a dolomitic calcite, since it is less deeply etched than that next the cobaltite. To the left is a small light gray area which represents the fringing cobaltite of another arborescent mass.

Fig. 10. Represents the same structure as Fig. 9, i.e., calcite filling the space between two closely arborescent masses, except that the envelope of niccolite is thicker and the cobaltite thinner than before. It should be noted that the vein-like appearance is very deceptive, suggesting that the breithauptite had been deposited massive, had subsequently been fractured, and in the cracks thus formed, niccolite, cobaltite and calcite had been deposited in order, as in a ribbon vein. This, however, is not the case. None of these minerals in reality penetrates the breithauptite, and fracturing did not occur until calcite had been deposited. The structure is due entirely to the closely arborescent form of the breithauptite, upon which the niccolite and cobaltite were precipitated. (x 70).

In all the specimens examined the same general relationship was found to hold; i.e., the aborescent breithauptite is entirely surrounded by a layer of niccolite which in turn bears a thin coating of cobaltite. On dissolving out the calcite which fills the intervening spaces, the outer surface of the cobaltite next the calcite is often seen to be crystallized in the form of brilliant cubes. In the specimens richest in breithauptite the layer of niccolite and cobaltite are relatively very narrow, typically

not over one millimetre thick and often very much less, with arborescent breithauptite closely set and with little intervening calcite. Other specimens show relatively small patches of breithauptite surrounded by a ground mass of niccolite as though the breithauptite had been the nuclei around which comparatively large quantities of niccolite had precipitated. The specimens richest in cobaltite are characterized generally by rather small and scattered breithauptite areas with calcite more prominent. When native silver occurs it appears to fill cracks which penetrate all the minerals just mentioned.

*Micro-structure of Breithauptite.*—After etching with nitric acid the breithauptite appears as a dark porous massive surface containing numerous minute irregular inclusions of niccolite which stand in bright relief (Fig. 8). The breithauptite areas with their coating of niccolite and cobaltite and the calcite filling in the spaces between this arborescent complex may be seen in Figures 9, 10 and 11. No inclusions of any mineral other than niccolite were observed in the breithauptite,

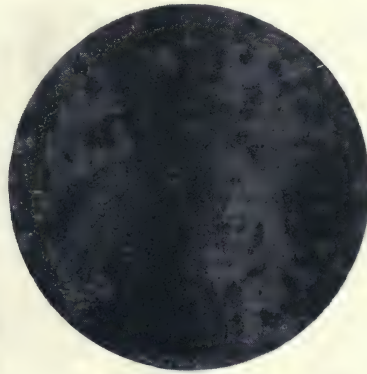


Fig. 11. The same structure as shown in Fig. 9. A few dark breithauptite inclusions in the niccolite may be noted. As before, the black vein-like band represents deeply etched calcite. (x 50).

which with this exception appears to be quite uniform and pure. Neither breithauptite nor niccolite exhibit any evidence of crystal form or structure. These structures suggest a simultaneous precipitation of breithauptite and minor quantities of niccolite as the first of the minerals to be deposited.

*Micro-structure of the Niccolite.*—The niccolite, which occurs as a narrow coating on the breithauptite appears to be quite pure, and has the closely granular appearance typical of a pure metal or mineral. In the more massive areas it contains inclusions of breithauptite which here also tend to be arborescent and appear to have been the nuclei around which the niccolite was deposited (Fig. 12). It also contains inclusions of cobaltite (Fig. 13). From the structures seen in Figs. 9, 10 and 11 the niccolite seems to have come down in maximum quantity after the breithauptite had been entirely precipitated.

*Micro-structure of the Cobaltite.*—This mineral occurs as a thin coating on the niccolite (Figs. 9, 10 and 11). It appears to have an extremely fine granular structure and may at times contain a few small inclusions of niccolite. The surface next the calcite is sometimes crystallized in cubes as previously mentioned. From

its position as the outer layer of the arborescent masses it appears to be the last formed of the nickel-cobalt minerals.

Calcite fills in the spaces between the arborescent masses of breithauptite, niccolite and cobaltite, and hence is next in order of deposition after cobaltite. It appears to be the ordinary white variety with good cleavage in places and effervesces readily with cold dilute hydrochloric acid. Some portions are more dolomitic, however, as may be seen by reference to Fig. 9, where the calcite next the cobaltite has been etched deeper than the central parts. A few small grains of quartz occur with the calcite. Minute slender prisms of ruby silver were seen embedded in the calcite between the nickel-cobalt minerals. They were too small for measurement or analysis.

Veinlets of native silver fill irregular cracks that at times penetrate all the nickel-cobalt minerals as well as the calcite (Figs. 14, 15). Occasionally silver may be seen filling cleavage cracks in the calcite, a good example of which is shown in



Fig. 12.

Fig. 12. Two skeleton-like areas of light-coloured breithauptite set in a dark ground mass of porous niccolite. (x 50).

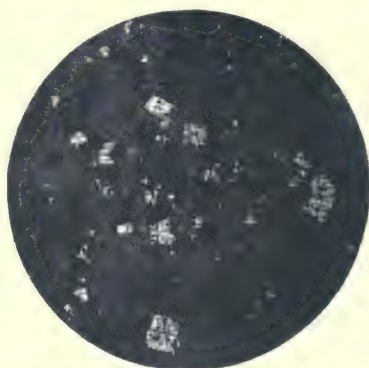


Fig. 13.

Fig. 13. Cubes of cobaltite in bright relief included in a ground mass of dark, somewhat porous niccolite. The darkest spots represent cavities in the niccolite. (x 50).

Fig. 16. These structures would seem to indicate that subsequent to the deposition of calcite there was a slight movement which caused more or less fracturing in all the minerals and developed cleavage cracks in the calcite. In these fractures and cleavage cracks the native silver was deposited.

*Summary:* From the structural evidence, it appears that breithauptite was the first mineral deposited accompanied by relatively small amounts of niccolite as microscopic included grains. After the precipitation of breithauptite had ceased the niccolite continued to come down and formed a thin layer over the arborescent breithauptite. On the niccolite was deposited a thin coating of cobaltite with the outer surfaces partly crystallized. Thus both niccolite and cobaltite were moulded upon the breithauptite. The deposition of the nickel-cobalt minerals then ceased and the spaces between the arborescent masses were filled with calcite. Then came a period of movement with a slight fracturing of the minerals, and finally native silver was deposited in the cracks thus formed.

The order of succession of the minerals studied would seem to indicate broadly three periods of deposition as follows:—

- I. Period of deposition of nickel and cobalt minerals, the nickel minerals being first.
  1. Breithauptite with minor amounts of niccolite as inclusions.
  2. Niccolite.
  3. Cobaltite.
- II. Calcite with perhaps a little ruby silver. Period of slight movement and fracturing.
- III. Native silver.

### Separation of the Minerals for Analysis

It became evident from microscopic examinations after etching that the nickel and cobalt minerals were so intimately associated as to render of doubtful value any analysis of merely hand-selected material. The separation of the minute niccolite inclusions from the breithauptite and of the breithauptite and cobaltite inclu-

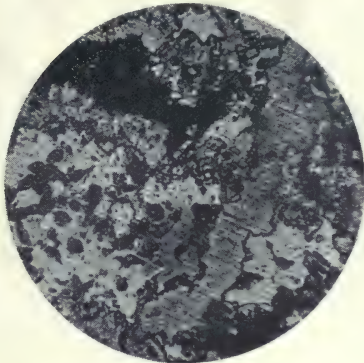


Fig. 14.

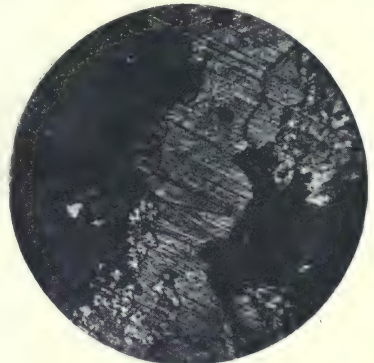


Fig. 15.

- Fig. 14. A veinlet of scratched native silver is shown cutting through two masses of the nickel-cobalt minerals and the calcite which fills the space between them, proving conclusively that it was the last mineral deposited. The light granular mineral in high relief is niccolite, the dark spots intermingled with the niccolite represent breithauptite. Cobaltite, as usual, fringes the niccolite as the fine-grained, light gray mineral next the black calcite. Some of the best examples of this structure were too large to photograph. (x 60).
- Fig. 15. Another example of a silver veinlet cutting the light-coloured nickel cobalt minerals at the top and bottom, and dark calcite to the right and left. (x 60).

sions from the niccolite was manifestly impossible by any mechanical means. In this connection the following paragraph from Campbell and Knight is here particularly applicable:

From the above (a photomicrograph showing microscopic inclusions in smaltite) it is seen how an apparently homogeneous mineral varies from the centre to the outside and also contains other minerals as impurities so finely distributed through it that complete mechanical separation would be impossible. We can also understand how in this way analyses would vary as recorded by Dana.<sup>15</sup>

An attempted separation by means of the electro-magnetic concentrator proved unsuccessful, and since mechanical separation was out of the question, it occurred

<sup>15</sup> Microscopic examinations of the Cobalt-Nickel arsenides and Silver deposits of Temiskaming—Economic Geology, September-October, 1906.

to the writer that a separation might be effected by the prolonged application of the etching methods previously outlined.

The behaviour of a mineral with acids when intimately associated with another mineral is sometimes not the same as when it alone is treated under similar conditions with the same acids. An instance of this is recorded by V. Goldschmidt and A. L. Parsons as follows:

By treatment with dilute hydrochloric acid the calcite can be dissolved out without the goethite being in the least attacked, so long as the least trace of the calcite is present.<sup>10</sup>

This fact was also noticed by the writer in the case of the association of minerals under discussion. It was found, for example, that aqua regia rapidly dissolves breithauptite and niccolite, leaving the cobaltite apparently quite unattacked so long as breithauptite or niccolite is present, but as soon as the two former minerals have disappeared, the cobaltite is at once vigorously attacked and quickly dissolved. Thus the cobaltite can be completely separated from the breithauptite and niccolite.



Fig. 16. White native silver filling cleavage cracks in dark calcite. This structure terminates an irregular, much thicker vein, the end of which is seen at the lower right-hand corner.

Similarly, though both niccolite and breithauptite alone are violently attacked by concentrated nitric acid, yet when the two minerals together are acted on by this acid the niccolite is relatively little attacked so long as a clean surface of breithauptite is present. Under the conditions described under etching methods, this process thus affords a means of freeing niccolite of breithauptite inclusions but not of cobaltite, which resists nitric acid so long as breithauptite or niccolite is present. Cobaltite, when alone, however, is readily attacked and quickly dissolved by nitric acid.

Finally, hot dilute nitric acid (1-4) dissolves away the niccolite leaving breithauptite practically unaltered, so that in this way we can free the breithauptite from niccolite inclusions. Here, again, when the niccolite has almost or quite disappeared, the solubility of the breithauptite in the dilute nitric acid is apparently much increased.

The details of the application of these methods are described below.

<sup>10</sup> Über Goethit von V. Goldschmidt und A. L. Parsons—Zeitschrift für Kristallographie usw. XLVII. Band, 3 Heft.

*Isolation of Breithauptite.*—A specimen containing as little niccolite and cobaltite as possible and with relatively large and pure-looking areas of breithauptite was selected and sawn into slices about an eighth of an inch thick. These slices were then treated with hot dilute nitric acid (1-4) until the outside coating of niccolite had been dissolved away and the slices presented the appearance of arborescent skeletons of breithauptite. The cobaltite falls off as the supporting niccolite is dissolved, leaving the breithauptite free of all impurities except the microscopic niccolite inclusions still contained in the interior. These thin branching pieces of breithauptite were then broken up by hand and inspected for freedom from niccolite and cobaltite. In this way about seven grams of breithauptite were obtained which apparently were entirely free of cobaltite and free of all but microscopic inclusions of niccolite. The specific gravity of this sample was 8.14 at 20° C. The arsenic content was 5.83 per cent. These selected pieces were then broken to 100 mesh and again treated with dilute nitric acid until the breithauptite began to be noticeably attacked as shown by the formation of the white antimony oxide. The breithauptite in the form of fine grains of size considerably less than 100 mesh was then rinsed and treated with dilute hydrofluoric acid to clear off any oxidised material, rinsed again and dried with alcohol at 120° C. Under the microscope the rounded grains thus obtained appeared to be of good colour, lustrous and apparently unchanged by the acid, though the sample in bulk was slightly darker than the original massive material. No cobaltite was visible. The specific gravity of the sample of about three grams was 8.23 at 20° C, but allowance must be made for the finely divided condition of the sample which results in slightly too high a figure for the specific gravity.<sup>17</sup> This material was then analyzed with the following results:—

Ni	Co	Fe	Sb	As	S	Total
32.09	.59	.04	66.62	.58	nil	99.92

It may be noted that the amount of nickel found is relatively a little low. This may be due to loss in analysis or to a slight surface oxidation of the breithauptite by the acid by which the bases are subtracted leaving a film of antimony oxide on the grains. As to the chemical constitution of the breithauptite, it seems probable that the cobalt and iron present replace some of the nickel since there is no microscopic evidence of the presence of cobaltite, while the absence of sulphur is a further confirmation. As to what extent arsenic actually replaces antimony, it is difficult to decide. The remainder of the material, after the analysis was subjected to further treatment with dilute nitric acid, was analyzed and the arsenic re-determined and found to be 0.47 per cent., which indicates that some niccolite was still present. This exhausted the supply of material. It is probable, however, that isomorphous arsenic, if present, amounts to less than 0.47 per cent.

The above analysis shows that the breithauptite is individually quite pure; in fact, this is nearer a theoretical analysis than any given by Hintze or Dana. It also

<sup>17</sup> Day, Allen and Iddings—The Isomorphism and Thermal Properties of the Feldspars. Pages 56, 57.

demonstrates that the chemical separation was in a large measure successful though for lack of material the niccolite was probably not entirely eliminated.

The following results were obtained on material from the same specimen:—

1. Hand-picked grains between 20 and 40 mesh selected for purity:—arsenic content = 11.23 per cent.
2. Grains with outer coating of niccolite removed by dilute nitric acid but still containing microscopic niccolite inclusions in the interior:—arsenic content = 5.83 per cent.
3. Material reduced to 100 mesh and again treated with dilute nitric acid:—arsenic content = 0.47 per cent.

The fact that this breithauptite though apparently pure and homogeneous to the naked eye contains nevertheless over five per cent. of arsenic, as microscopic niccolite inclusions is evidence of the importance of a microscopic examination of minerals which are to be submitted to analysis, since it may settle the question as to whether the presence of certain elements is due to isomorphous replacements or to admixture with another mineral in which they are contained.

*The Isolation of Niccolite.*—One of the largest, purest specimens containing relatively little breithauptite was sawn into slices about one sixteenth of an inch thick which were treated with concentrated nitric acid containing tartaric acid as previously described under etching methods. When all the breithauptite that could be reached by the acid had been removed, the pieces were broken successively to 20, 40, 60, 80 and 100 mesh and retreated after each sizing. In this way it was hoped that the breithauptite inclusions would be eliminated. The sample was finally treated with hydrofluoric acid to clear off oxides, rinsed and dried at 120° C. Under the microscope the grains appeared bright, clean and of good colour. The sample, however, still contained brilliant cubes of cobaltite which apparently had scarcely been effected by the acid.

Considerable experimenting had previously been done with a view to finding some re-agent which would dissolve the cobaltite without affecting the niccolite or breithauptite, but all these attempts proved unsuccessful. There is, therefore, no means of determining absolutely whether any of the nickel is replaced by cobalt in this niccolite. Analysis of the sample thus prepared yielded the following results:—

Ni	Co	Fe	As	Sb	S	Total
40.64	2.04	trace	50.78	4.95	1.47	99.88

Specific gravity of the sample at 20° C = 7.66.

The remainder of the sample after analysis was re-treated with acid and the final determination yielded 3.81 per cent. of antimony. From the result it would appear that the material analyzed still contained breithauptite, and the amount of possible replacing antimony is thus reduced to less than 3.81 per cent., though it seems likely that most of this represents breithauptite.



Since sulphur is present in excess of the amount required to combine with the cobalt to form cobaltite, we must assume the presence of isomorphous sulphur to the extent of 0.37 per cent., if we consider all the cobalt to exist as cobaltite of theoretical composition.

Here again in the case of niccolite is demonstrated the usefulness of a microscopic examination. We know definitely that any antimony in excess of 3.81 per cent. exists as breithauptite, and also that a large proportion of the cobalt is present in the form of cobaltite.

A determination of antimony is 20-40 mesh grains of niccolite from the same specimen, carefully selected by hand and in which no breithauptite was visible to the naked eye yielded 17.76 per cent. Had there been no microscopic examination this would probably have been reported as an arite with the above percentage of antimony replacing arsenic. Thus it is possible that certain so-called arites may be in reality relatively pure niccolite containing minute inclusions of breithauptite. Similarly a sample of breithauptite containing a high percentage of very minute niccolite inclusions might also be reported as arite, though the enclosing breithauptite itself might be almost of theoretical purity. In this way an entirely fictitious series of arites containing any proportion of arsenic and antimony might be obtained.

*Isolation of Cobaltite.*—Examination of the hand specimens showed that those in which the calcite gangue was relatively prominent with the breithauptite as rather small and scattered areas, were richest in cobaltite. Such a specimen was selected, reduced to 40 mesh and after the calcite had been dissolved out was treated with aqua regia. In this way the breithauptite and niccolite were dissolved away, leaving the cobaltite as a relatively very small amount of finely divided residue. As previously noted, the cobaltite is apparently scarcely acted on until the breithauptite and niccolite have disappeared. It was found that the cobalt residue contained no nickel, so that the very delicate dimethylglyoxime test could be used to ascertain when all breithauptite and niccolite had been removed. When fresh quantities of the aqua regia solvent, therefore, no longer reacted for nickel, the separation was complete and the residue was washed, dried and examined under the microscope. The whole amount readily passed the 100 mesh. It was seen to consist partly of material without crystal form, derived, no doubt, from the layer coating the niccolite, and partly of very perfect cubic crystals which still retained their sharp edges and corners and brilliant metallic lustre. Accompanying the cobaltite were grains of yellow, rose-coloured, white and colourless quartz derived from the calcite gangue, and a few minute particles of silver. In order to get rid of the quartz grains the residue was treated with hydrofluoric acid until they were all dissolved. This was followed by dilute nitric acid to dissolve the silver.

In this way about three grams of apparently pure and in part crystallized material were obtained. The sample had a specific gravity of 6.35 at 20° C.

Analysis of this material dried at 120° C. yielded the following result:—

CO	Ni	Fe	As	S	Ag	Total
34.83	nil	.63	46.97	17.48	.04	99.95

From the above analysis and its cubic crystallization the mineral appears to be cobaltite, which has the theoretical composition: Co. 35.5, As. 35.2, and S. 19.3 per cent. The small amount of silver present was doubtless due to the escape of particles of native silver not affected by the nitric acid.

It will be noted that the arsenic is in excess of the theoretical percentage, while the sulphur falls below. This may result from replacement of sulphur by arsenic or may be due to the presence of small quantities of skutterudite,  $\text{CoAs}_3$ . The somewhat high specific gravity of the sample rather favours the latter explanation. To settle this point absolutely would require a relatively large sample of the cobaltite residue, which would necessitate the destruction of several pounds of the original specimens. There would then still remain the difficult problem of isolating the supposed skutterudite from the cobaltite.

However, the fact remains that cobaltite is, in any case the important constituent of the material analyzed. Further, it is remarkably pure as compared with most of the analyses given by Hintze and Dana. Iron is present in very small amount, and the entire absence of nickel as shown by the dimethylglyoxime test on one gram of material is especially noteworthy, since from its close association with niccolite and breithauptite it might be expected to contain nickel replacing cobalt.

#### **General Conclusions Regarding Breithauptite and Associated Minerals**

The methods of chemical separation adopted as a result of observation of the relative etching effects of various acids have proven successful except in the case of cobaltite inclusions in niccolite.

That the three minerals, breithauptite, niccolite and cobaltite, though so very closely associated as to suggest simultaneous precipitation, especially in the case of breithauptite and niccolite (Fig. 8), nevertheless individually possess almost their respective theoretical compositions with but very little possible replacement by isomorphous elements, would indicate the possibility of the wide variation in some mineral analyses being due more to admixture with other minerals than to actual replacement with isomorphous elements.

#### **Smaltite and Chloanthite Crystals, Foster Mine**

A specimen of what appeared to be very pure smaltite from the Foster mine showed good crystals embedded in a hard dolomitic gangue. The crystals are slightly distorted cubes with small octahedral and still smaller rhombic dodecahedral faces. Some of the cubes reach a size of 5 millimetres.

It was thought that it would be interesting to see if these crystals were intergrowths like those described by Baumhauer, and analyzed by Vollhardt. One of the cubes was cut through the centre and polished parallel to a cubic face. After etching with acid it was seen to be made up of two different materials which were intergrown as shown in Fig. 17. On further etching at least two other components could be recognized but these were present only in very small amount. The massive part of the specimen was also etched and showed the same two prominent materials (Fig. 18) together with small quantities of others not identified. On prolonged etching the inner part of the growths was corroded deeper than the outer later part and relatively much nickel passed into solution, so that the central areas are

probably essentially chloanthite. There are also extremely minute inclusions in the chloanthite which can be seen only with a high power.

A single analysis was made on crystals with the following results:

Co	Ni	Fe	Cu	As	S	Total
13.81	11.35	1.21	.96	71.61	.75	99.69

A sample of the more massive, but partially crystallized material was prepared in order to try some separation experiments. This sample on analysis yielded the following results:

Co	Ni	Fe	Cu	As	S	Total
12.16	14.14	2.10	.40	66.87	4.13	99.80

Co: Ni: Fe = 5.79 : 6.73 : 1

Theoretical composition of smaltite—Co 28.12 and As 71.88 per cent.  
 “ “ of chloanthite—Ni 28.12 and As 71.88 per cent.

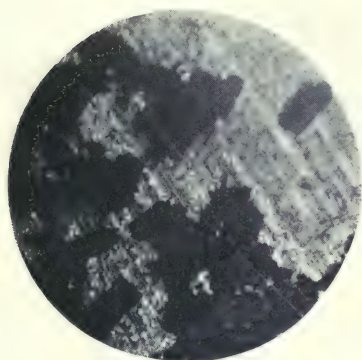


Fig. 17.

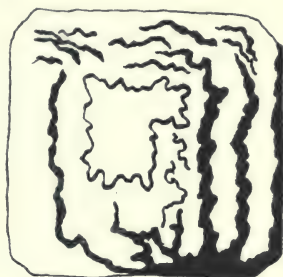


Fig. 18.

Fig. 17. Intergrowth of smaltite and chloanthite in a crystal about 2 millimetres in diameter (x 50).

Fig. 18. Sketch showing major features of smaltite-chloanthite intergrowth in a crystal 2 mm. in diameter as seen under the low power.

It is evident that both the crystals and the more massive material consist of about equal parts of smaltite and chloanthite.

A sample after prolonged treatment with hydrochloric acid and potassium chlorate, yielded a residue from which the following amounts were obtained:—

Co = .0868 g, Ni = .0064 g, Fe = .0098 g or

Co : Ni : Fe = 8.857 : 0.65 : 1

It is evident that this residue was nearly pure smaltite.

Another sample was agitated with successive quantities of silver nitrate solution and the solutions thus obtained were analyzed.

First solution yielded Co = .0068 g, Ni = .0393 g, Fe = .0018 g or

Co: Ni: Fe = 3.77: 21.83: 1

Second solution yielded Co = .0409 g, Ni = .0222 g, Fe = .0080 g  
 Co: Ni: Fe = 5.11: 2.77: 1

Third solution yielded Co = .0686 g, Ni = .0173 g, Fe = .0113 g or  
 Co: Ni: Fe = 6.07: 1.53: 1

These experiments serve to show that silver nitrate solution acts more readily on chloanthite than on smaltite, but as a separation method the large amount of silver precipitated is a disadvantage as it tends to retard the action of the solution, which becomes very slow as the amount of silver increases.

The results obtained seem to indicate that a smaltite residue containing little or no nickel might be obtained by sufficiently prolonged application of suitable separation methods.

*Paragenesis*—Considering first of all, the intergrowths which occur as good crystals, it seems probable that the crystals grew continuously from a mother solution which contained the elements of both smaltite and chloanthite, and that both these minerals were being precipitated as the crystals grew. The absence of definite concentric or zonal structure renders it unnecessary to suppose that the crystals were formed by overgrowth due to sharp changes in the cobalt and nickel content of the solution. A study of the massive part, however, seems to indicate that chloanthite was formed in greatest quantity during the early stages. The chloanthite areas are not pure but contain minute inclusions which are probably smaltite, and are bordered by smaltite. Apparently chloanthite was predominantly precipitated at first, and smaltite slightly later, but the two periods overlap.

*Summary*—The crystals examined are not homogeneous mixed crystals of cobalt-nickel diarsenide, but are intergrowths of about equal parts of smaltite and chloanthite, which appear to have been precipitated together. Chloanthite is doubtless much more common at Cobalt than has been supposed as a constituent of massive smaltite ore, and in the aggregate may be responsible for a greater part of the nickel content of Cobalt ores than the more conspicuous niccolite.

#### **Cobaltite Crystals, Columbus Claim**

The crystals which have been found at this mine are probably not surpassed in perfection of development by those of any other known locality. They are essentially octahedral in habit, with relatively small cube faces. A small percentage have the cube and octahedron about equally developed but in the great majority the octahedron predominates.

One of the crystals—an octahedron with small cube faces—measures 7 mm. between cube faces.

These crystals have been analyzed by J. S. De Lury<sup>18</sup> and found to contain notable amounts of iron and nickel. Remembering the slight solubility of cobaltite relative to the more common arsenides, which was displayed in the separation of minute cobaltite crystals from niccolite and breithauptite and also bearing in mind the very small capacity of this mineral for precipitating silver from silver sulphate solutions, noted by Palmer and Bastin,<sup>19</sup> the writer decided to subject

<sup>18</sup> Cobaltite Occurring in Northern Ontario, Canada, by Justin S. De Lury—*American Journal of Science*, Vol. XXI, April, 1906.

<sup>19</sup> Metallic Minerals as precipitants of silver and gold, *Economic Geology*, Vol. 8, No. 2, March, 1913.

samples of this cobaltite to the action of such re-agents as might be expected to act more rapidly on any iron or nickel minerals that may be present as microscopic inclusions.

A preliminary microscopic study of etched surfaces of these crystals revealed numerous inclusions which it was thought might be sufficient in amount to account for the iron and nickel found in the analysis. For instance, a very perfect crystal which showed no evidence whatever of inclusions, externally, was cut through the centre parallel to a cubic face. In this case inclusions of at least two different minerals were observed. On being strongly etched with concentrated hydrochloric acid and potassium chlorate, one kind of inclusion is strongly attacked while another kind appears to be even more resistant than the cobaltite itself (Fig. 19). Some of the

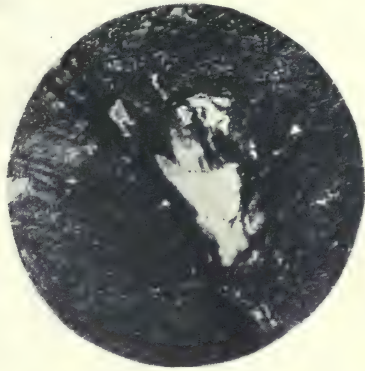


Fig. 19. Inclusions of gersdorffite (?), light, in relief, in ground mass of a cobaltite crystal. Another sort of inclusion has been deeply corroded and is represented by the black line crossing the picture.

inclusions occur as wandering lines which can scarcely be fractures, since in some cases, they have a roughly concentric arrangement. On the other hand, unmistakable mineral-filled fractures are present in some of the other crystals. The inclusions that appear to be more resistant than the cobaltite are scattered throughout the cobaltite groundmass in irregular grains which remain bright and unattacked, even when the cobaltite has been roughened and the more soluble inclusions deeply corroded by the strong acid.

The structure suggests that most of the inclusions were formed at the same time as the cobaltite and that there is good ground for believing that the iron and nickel found by analysis are due to mineral inclusions rather than to isomorphous replacement of cobalt by nickel and iron.

A sample of about 5 or 6 grams of crystals, free from adhering matter was selected, ground to 200 mesh and analyzed, with results as in No. 1.

	Co	Ni	Fe	As	S	Total
I	28.11	3.07	4.76	44.61	19.57	100.12
II	28.28	3.12	4.40	44.82	19.20	99.82
III	28.64	3.06	4.11	44.77	19.34	99.92
Theoretical.	35.41	....	....	45.26	19.33	100.00

The powder left after analysis No. 1, was digested for two or three days at room temperature with concentrated hydrochloric acid, a little potassium chlorate being added from time to time. The residue was then washed, dried and a sample analyzed, which gave the results under No. II. What remained was digested with silver nitrate solution for a week. Only a very little metallic silver was precipitated, which was removed with dilute nitric acid. The final residue gave the results under No. III. In the analyses, Co, Ni, Fe, and S were determined only once, the arsenic by titrations of two aliquot portions of the same sample.

The chief results of interest are:

1. The regular increase in the amount of cobalt found, with corresponding decrease in the percentage of iron.
2. The fact that the nickel percentage remains practically the same, or perhaps even increases slightly. This result, considered along with the observation of inclusions which appear to resist corrosion better even than cobaltite, appears to point to the conclusion that there is some inert nickel mineral present, intergrown with the cobaltite. It is not unlikely that this mineral is gersdorffite—NiAsS. The progressive decrease in the iron found tends to confirm the suspicion that the iron is present as a mineral rather than in molecular combination replacing cobalt.

*Summary*—All the evidence—microscopic and analytical—confirms the conclusion that in the case of these cobaltite crystals, the iron and nickel found by analysis can be accounted for by the presence of microscopically visible inclusions of other minerals in the crystals.

There is reason to believe that these included minerals are, for the most part, not later infiltrations or replacements, but are intergrowths with cobaltite, being formed from the same solution at the same time.

#### Löllingite, Kerr Lake Mine

The specimen in which this mineral was identified is a cross-section of a portion of a calcite vein. One side was originally in contact with the vein wall and contains small angular fragments of decomposed country rock (Figs. 20 and 21).

The vein shows white calcite of two generations (A) and (B), of which (A) appears to be the later, since the base of the löllingite growths (L) rests on (B) and their partially crystallized terminations are embedded in (A). The calcite (B) has a slightly bluish tinge and is readily distinguishable from (A) which is

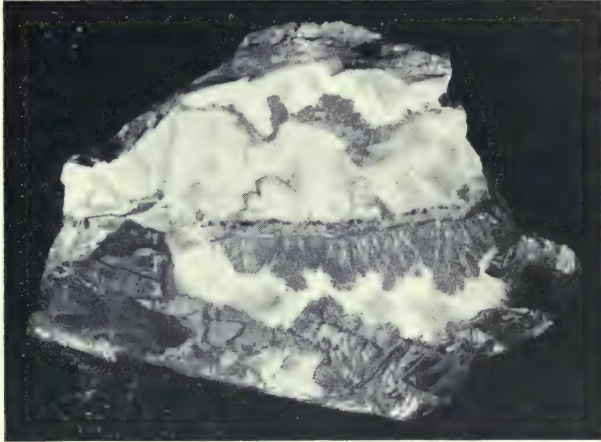


Fig. 20. Löllingite specimen (natural size).

almost pure white. The löllingite shows a marked fibrous structure with the fibres somewhat radiating, but in a general way normal to the vein walls. Extremely minute fractures filled with calcite traverse the löllingite masses.

On dissolving away the calcite with hydrochloric acid, the löllingite, which is not attacked so long as a little calcite remains, is obtained as radiating fibrous

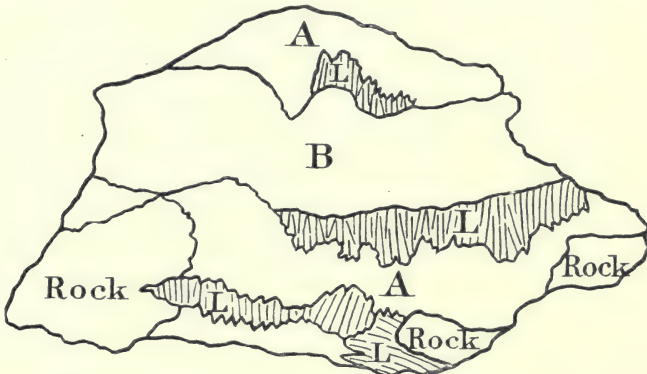


Fig. 21. Diagram of löllingite specimen (natural size).

botryoidal masses. The surface which was embedded in calcite (A) has a velvety appearance and reflects light from very numerous minute sparkling points, which under a microscope are seen to be crystal faces.

Using a binocular microscope, the surface appears to be made up of very small terminated crystals showing minute faces. An attempt to remove some of these for measurement proved fruitless. A few small crystals of arsenopyrite up to .5 mm. diameter are embedded in or attached to the surface.

Examination of polished surfaces etched by acid (Fig. 22) indicates that certain parts are more readily attacked than others, and that the material is far from homogeneous. After a rather severe etching one set of fibres stands in sufficient relief to be repolished by lightly rubbing on fine emery paper, while another constituent is so deeply corroded that it is not affected by moderate rubbing. In fact, three different minerals can be distinguished with certainty, and there are indications of a fourth. The two most important constituents, as will be seen from the analysis, are löllingite ( $\text{FeAs}_2$ ) and cobalt diarsenide. The latter, because of the high specific gravity and the fibrous character of the intergrowth, is probably the rhombic form, safflorite. The arsenopyrite previously noted seems to be most abundant toward the outer portions of the growths.

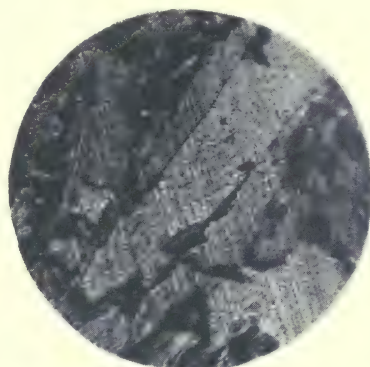


Fig. 22. Löllingite surface strongly etched, showing three constituents. Two are bright and stand in relief. The third is deeply etched and appears black in the picture. (x 50).

*Analysis*—At first only a small sample of about two grams was selected which yielded the following results:

	Fe	Co	Cu	As	S	Sb	Ni	Total
Per cent.	22.18	5.62	.41	70.84	.82	trace	absent	99.87
Mol. Ratio	.3972	.0979	.0064	.9448	.0256	....	....	....
Arsenopyrite Fe As S	.0256	....	....	.0256	.0256	....	....	....
Safflorite Co As <sub>2</sub>	....	.0979	....	.1958	....	....	....	....
Löllingite Fe As <sub>2</sub>	.3617	....	....	.7234	....	....	....	....
Excess	.0099	....	....	....	....	....	....	....

For convenience, the calculations have been made on the assumption that löllingite, safflorite and arsenopyrite of theoretical composition are present. The sulphur has all been calculated as arsenopyrite, but, as will be seen later, there is reason to believe that some of it should be assigned to the copper.



Another sample of about 7 grams was selected with a view to trying some of the separation methods used in other instances. The specific gravity of the sample before grinding was 7.300 at 15.5° C. This sample on analysis gave the following results:

	Fe	Co	Cu	As	S	Sb	Ni	Total
Per cent.	23.60	5.94	.38	69.08	.96	trace	absent	99.96
Mol. Ratio	.4227	.1007	.0059	.9212	.0299	....	....	....
Arsenopyrite (Fe As S)	.0299	....	....	.0299	.0299	....	....	....
Safflorite (Co As <sub>2</sub> )	....	.1007	....	.2014	....	....	....	....
Löllingite (Fe As <sub>2</sub> )	.3449	....	....	.6899	....	....	....	....
Excess	.0479	....	....	....	....	....	....	....

$$\text{Fe} : \text{Co} = 1 : 0.251$$

Compared with the first analysis, this one shows that the mass varies somewhat in composition from place to place, thus confirming the conclusions arrived at by microscopic examination, that the material is an intergrowth of distinct minerals.

As only a small amount of material was available the separation experiments were carried out on about 5 or 6 grams. Only iron and cobalt were determined.

Exp. 1. Concentrated hydrochloric acid with a little potassium chlorate on 250 mesh powder. The filtrate contained relatively much copper.

.0226g Fe and .0054g Co, or Fe: Co = 1: 0.237.

Exp. 2. Silver nitrate solution on 250 mesh powder, filtrate contained .0307 g Fe and .0075 g Co or Fe: Co = 1: 0.244.

Exp. 3. Nitric acid (1 : 1) on 250 mesh powder, filtrate contained .0852 g Fe and .0163 g Co or Fe: Co = 1; 0.191. This treatment was continued and the final residue yielded .1363 g Fe and .0635 g Co or Fe: Co = 1: 0.267.

These experiments for lack of sufficient material could not be carried far enough to obtain definite separations and their value is also lessened because sulphur was not determined, as at that time the arsenopyrite had not been recognized, and it was thought that löllingite and safflorite were the only important variables, whereas, there are certainly three, and possibly five, minerals present. There seems to be, however, no great difference in the solubility of the minerals when in the form of a fine powder, except that the copper mineral, whatever it may be, seems to be more readily attacked than the others. This probably is because the minerals, being closely related chemically and crystallographically, have only small differences in solubility and potential. Furthermore, when finely powdered, the electrical contact between the mineral protected and the protecting mineral is

not so good as in the case of a polished surface, and isolated particles of the protected mineral which do not have some of the protecting mineral attached to them will readily dissolve.

*Paragenesis*—In a complex intergrowth of this sort it is impossible to separate different periods of precipitation. The growth of the various minerals has been, not in bands parallel to the direction of the vein, nor in concentric layers as we might expect if the mother solution varied in composition from time to time, but in a fibrous aggregate approximately normal to the vein wall and containing the individual minerals side by side. Apparently all the mineral constituents were being formed continuously during the whole period of precipitation, though the percentage of arsenopyrite appears to have increased toward the last. A rather slow, contemporaneous precipitation of the different minerals from a solution of fairly constant composition appears to be the most reasonable explanation of the formation of such an intergrowth.

*Summary*—There is good reason to credit the cobalt found in the analysis to safflorite. Arsenopyrite crystals were identified by blow-pipe tests and hence the sulphur may be assigned, in part at least, to arsenopyrite. The copper comes off in greatest quantity at first in separation experiments, and probably is present as an easily soluble compound with sulphur. The chief mineral constituent is löllingite.

In short, the material examined appears to be an extremely intimate intergrowth of several minerals closely related, chemically and crystallographically. It is not a single homogeneous mineral containing isomorphous replacing elements in molecular combination. On the other hand it has not been proved that the individual mineral components themselves are not subject to molecular replacement by isomorphous elements.

### Arsenopyrite Crystals, O'Brien Mine

Crystals of arsenopyrite from Cobalt have been described and illustrated in Part II. of the Nineteenth Report of the Ontario Bureau of Mines.

The writer in dissolving away the calcite from some of the so-called glaucodot of the O'Brien mine found a residue of detached crystals up to 2.5 mm. across, which it was thought might be glaucodot, but which analysis proved to be arsenopyrite.

The crystals are of a habit which is rather unusual for arsenopyrite, the base being most prominent, followed in order by the prism  $\infty$  (110), and small domes 01 (011) and 10 (101). The base gives multiple reflections and probably consists really of almost infinitely flat pyramids or domes. The drawing (Fig. 23) represents the type habit and characteristic development of the faces. The faces, especially the domes 01, 0 $\bar{1}$  are usually corroded, and only two crystals were found to give fairly good reflections. Besides the forms mentioned, which were definitely determined, there also occur corroded traces of the brachypinacoid and of a pyramid in the zone of the prism  $\infty$ . One crystal gave very poor readings for a prism which seems to be  $\infty \frac{1}{3}$ .

An analysis of the crystals yielded the following results:

	Fe	Bi	Co	As	S	Total
Per cent.	34.53	.79	.09	44.34	20.22	99.97

The analysis proves that these crystals are not glaucodot. The presence of bismuth is unusual, though it has been reported in two out of eighty-one analyses of arsenopyrite recorded by Hintze. When examined under a microscope, however, the crystals are seen to be non-homogeneous, which probably accounts for the corrosive effect of the acid on them, as pure arsenopyrite is not much affected by hydrochloric acid.

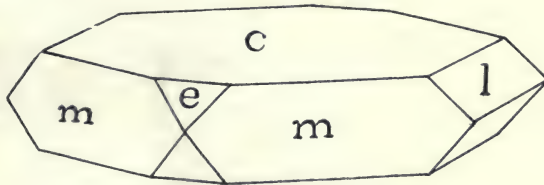


Fig. 23. Arsenopyrite crystal, G'Brien mine.

The finding of arsenopyrite as isolated crystals embedded in calcite and as crystals attached to the arsenide complex, shows that the main arsenopyrite precipitation was later than the main arsenide precipitation, though for a time both were probably being formed together. Bismuth also, in other instances, seems to come later than the period of maximum arsenide deposition, so that its presence here is not remarkable.

Arsenopyrite has been identified in a number of specimens from Cobalt and is probably present in relatively small quantity in most of the complex ore. When intergrown with massive cobalt-nickel diarsenide ore, it cannot be readily detected, except by examining etched surfaces.

#### Rammelsbergite, University Mine

This specimen at first glance appeared to consist chiefly of very pure niccolite bordered by a band of smaltite from a quarter to a half inch wide, in typical dolomitic vein calcite. On closer examination the supposed smaltite, which analysis shows to be really rammelsbergite, is seen to have the fibrous structure and prismatic cleavage which one associates with the rhombic cobalt-nickel arsenides.

Microscopic observation of etched surfaces shows that the rammelsbergite which is immediately in contact with the niccolite is crystallized, the numerous long, prismatic crystals extending into the niccolite (Fig. 25), and thus proving that the niccolite is the younger of the two.

The niccolite also contains detached crystals of rammelsbergite (Fig. 26) which, in some instances, have been fractured across and the fractures filled with niccolite. The rammelsbergite mass itself is not entirely pure as it contains small inclusions of niccolite which appear to have been precipitated at the same time, though in very much smaller quantity. The niccolite also contains inclusions of

what appears to be breithauptite and possibly of cobaltite, though the latter cannot be identified with certainty because of the nearly square cross-sections of the rammelsbergite crystals, which simulate the cubic crystals of cobaltite.

An analysis of the rammelsbergite yielded the following results:

	Ni	Co	Fe	As	S	Sb	Total
Per cent.	27.84	1.80	trace	67.32	2.03	.83	99.82

Specific gravity at 20°C = 7.157.

Theoretical composition of rammelsbergite, Ni = 28.12 per cent., As = 71.88 per cent.

The analysis indicates that the material is essentially nickel diarsenide. The slight excess of nickel and cobalt over the theoretical percentage is no doubt due

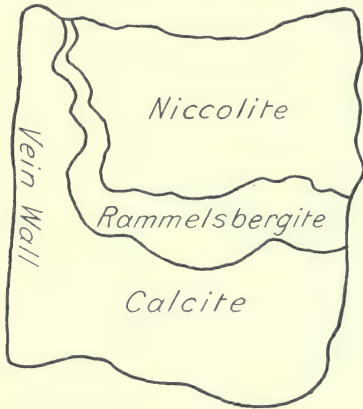


Fig. 24.

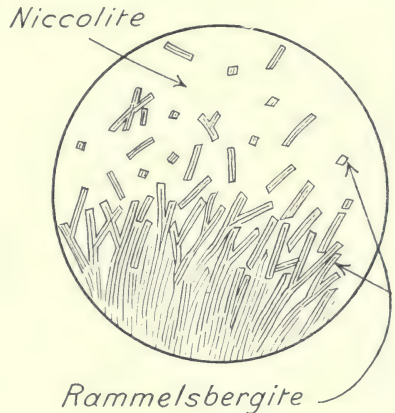


Fig. 25.

Fig. 24. Diagram of rammelsbergite specimen, natural size.

Fig. 25. Drawing of crystallized rammelsbergite at the contact with niccolite, as seen under the microscope.

to the presence of some niccolite, and the antimony is probably in the form of breithauptite associated with the niccolite. The rôle of the sulphur and cobalt is doubtful as cobaltite was not identified with certainty. The long prismatic crystals seen projecting into the niccolite together with the high specific gravity and the well-marked cleavage prove the mineral is the rhombic form—rammelsbergite.

*Paragenesis*—The fact that the rammelsbergite in contact with the niccolite is crystallized, with the crystals embedded in the niccolite would indicate that the niccolite is the later of the two. Such crystallized surfaces may often be seen in banded veins or vugs in which the growth has undoubtedly been from the walls inwards. The small inclusions of niccolite which occur in the rammelsbergite are probably due to simultaneous precipitation of a small amount of niccolite during the formation of the rammelsbergite. The composition of the mother solution which at first precipitated rammelsbergite with a little niccolite, must have altered in such a way that the amount of niccolite formed was increased until only a small amount of rammelsbergite was being precipitated along with the niccolite. At a

point about a quarter inch from the edge of the massive part of the rammelsbergite, only scattered, isolated crystals can be seen in the niccolite, which appears to the naked eye to be very pure.

That the structure just described could be due to replacement of either mineral by the other, appears to be improbable. If niccolite replaced rammelsbergite the crystals would have suffered more severely. They are, on the contrary, very perfect and entirely uncorroded. If rammelsbergite be supposed to have replaced niccolite one would have difficulty in explaining the presence of perfect, isolated crystals of rammelsbergite embedded in niccolite at considerable distances from the main rammelsbergite mass.

The relationship between rammelsbergite and niccolite thus appears to support the theory which will be developed later, of the general order of precipitation at Cobalt, i.e., diarsenides first, followed by monarsenides, these by sulpharsenides, and finally sulphides and disulphides, with native silver.

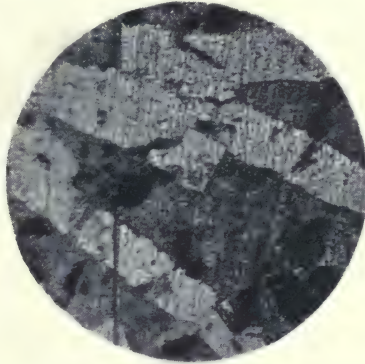


Fig. 26. Long prismatic crystals of rammelsbergite in niccolite.

#### Glaucodot, O'Brien Mine

Glaucodot has been mentioned as occurring at Cobalt, but its presence has not been proved<sup>20</sup>. Having examined a large quantity of the material from the O'Brien mine, which has long been supposed to contain glaucodot, the writer is satisfied that the complexity of the material is such that the presence of glaucodot cannot be confirmed. The reasons for this opinion will appear later.

On dissolving away the calcite from some of this material, numerous small tabular crystals up to 2 mm. in diameter were obtained. It was thought that these might be glaucodot. They were measured on the two circle goniometer, but, while the signals were not very good, the readings indicated that the mineral might be either arsenopyrite or glaucodot. They were then analyzed and found to be arsenopyrite, containing .09 per cent. of cobalt. Another lot of crystals of different habit proved to be arsenopyrite also.

The massive material was then examined by etching a number of polished surfaces, and it proved to be a very complex intergrowth of five or six different minerals, often in a very finely divided condition. Some of the larger structures can be seen with a hand lens, but the microscope shows that the whole is a mixture of grains,

<sup>20</sup> Pt. II, 19th Report, Ont. Bur. Mines, p. 22.

often of extremely small size, sometimes concentrically arranged (Fig. 27), sometimes irregularly distributed like the grains in a section of granite. The main constituents appear to be smaltite, arsenopyrite and pyrite with small amounts of what appears to be niccolite or breithauptite—perhaps both. On treating a fragment with hydrochloric acid till the arsenides are partly dissolved, a thin network of native silver is revealed.

A sample of the mass was analyzed with the following results:

	Ag	Co + small amount of Ni	Fe	Bi	Cu	As	S	Sb	Quartz	Total
Per cent	2.12	$\frac{17.34}{58.97} = .2941$	$\frac{10.28}{55.84} = .1799$	.95	.09	$\frac{60.77}{74.96} = .8106$	$\frac{8.08}{32.07} = .2520$	.47	.12	100.22

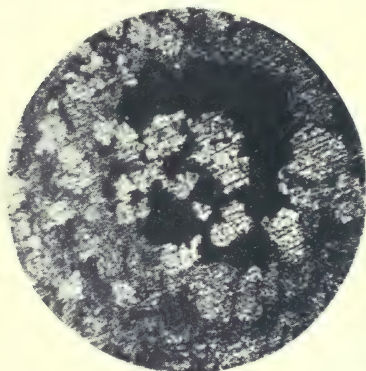


Fig. 27.

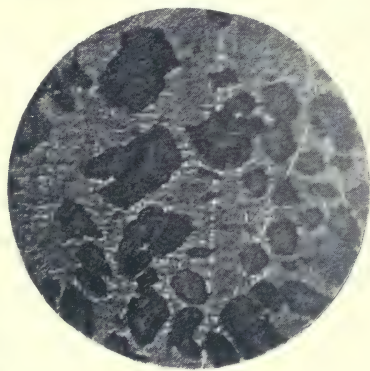


Fig. 28.

Fig. 27. Concentric structure, representing an intergrowth of several different arsenides. The black central part is more or less square in outline, suggesting a cube of smaltite or chloanthite.

Fig. 28. Matildite inclusions (dark), in light ground mass of galena.

This material serves very well as an example of the extreme microscopic complexity of much of the Cobalt ore. There appears to be no evidence, however, which would lead to the supposition that glaucodot is one of the constituent minerals.

After examining a considerable quantity of the massive material microscopically, another sample, which was apparently purer than the first lot, was selected and analyzed, with results as below:

	Co	Fe	Ni	As	S	Cu, Bi, Ag and Sb	Total
Per cent.	$\frac{17.22}{58.97} = .2920$	$\frac{10.79}{55.84} = .1933$	$\frac{1.80}{58.68} = .0307$	$\frac{63.14}{74.96} = .8422$	$\frac{6.75}{32.07} = .2105$	trace	99.70

The ratios here are much the same as in the first analysis, but smaller amounts of copper, bismuth and antimony are present. There is no evidence that glaucodot is one of the constituents.

*Summary*—The material is a complex microscopic intergrowth of several minerals, which are so intimately mixed that they cannot be definitely assigned to

different periods of precipitation though the arsenopyrite, pyrite and chalcopyrite were formed chiefly at the last. Cobalt diarsenide (smaltite or safflorite) and arsenopyrite with less pyrite or marcasite are the predominant minerals of the complex. Several others such as niccolite, löllingite, breithauptite are indicated by etching tests and analysis. Native silver and probably native bismuth and chalcopyrite are present in small amounts. There appears to be no reason to suppose that glaucodot is one of the constituents, knowing as we do that arsenopyrite and pyrite are present.

Here, again, all the facts point to slow simultaneous precipitation of several minerals from a solution which varied but slowly in composition, the sulpharsenides and sulphides predominating during the last stages of the deposition.

*Matildite—Galena intergrowth, O'Brien Mine.*

The specimen examined was a small mass of galena in which certain areas were remarkable because of their whiter colour and brighter lustre, and also because of a disturbance of the normal cubic cleavage which in such parts assumes a distorted, roughly rhombohedral form. Microscopic examination of an etched surface (Fig. 28) shows that this last material is an intergrowth of two distinct minerals, of which the ground mass is galena and the included mineral, as shown by the accompanying analysis, is matildite.

	Pb	Bi	Ag	S	Sb	Fe	Total
Per cent.	54.35	20.26	10.11	14.68	.45	.20	100.05
Mol. Ratio.	.2624	.0974	.0937	.4580	.0037	.0036	....
Galena Pb S	.2624	....	....	.2624	....	....	....
Matildite AgBiS <sub>2</sub>	....	.0937	.0937	.1874	....	....	....
Excess	....	.0037	....	.0080	.0037	.0036	....

Specific gravity at 21° C = 7.201.

The somewhat inexact ratios shown by the analysis may be due partly to the difficulties of the chemical separations. The rôle of the iron and antimony found is doubtful. It is evident, however, that the material is essentially an intergrowth of galena and matildite in the approximate proportion of: Galena 62.76, and Matildite, 36.50 per cent.

*Paragenesis.*—The specimen described was a small mass of the material associated only with galena and traces of calcite, so that it was impossible to ascertain the relationship of matildite to the common minerals of Cobalt.

Microscopic examination of etched surfaces shows that the intergrowth is of a very intimate and uniform character. Any section taken at random, throughout

the mass, shows the same characteristic structure. There is no arrangement of the matildite particles along cleavage lines or cracks in the galena as might be expected if the structure were due to metasomatic replacement of galena by matildite. That the perfect cleavage of galena persists in the intergrowth, though in a slightly distorted form, and the very fact that the cleavage is distorted so that it is no longer exactly cubic, along with the isolated, discontinuous character of the matildite inclusions, seems to the writer to be evidence as conclusive as can be expected of the simultaneous precipitation of the matildite and galena.

Further, in all occurrences of matildite recorded by Dana and Hintze from widely separated regions of the world, this mineral has been intimately associated with galena. All the analyses on record show a lead content, varying from 2.58 to 8.00 per cent., and in every case the lead has been reported by the analyst as galena. There are many examples of such pairs of minerals which very often occur as intergrowths, even when in crystals, as in the case of smaltite and chloanthite. Such intergrowths can hardly be explained in any other way than by supposing that the two constituent minerals were being formed continuously during the period of crystallization.

The fact that matildite from such widely separated localities as Peru, Colorado, Japan and Ontario is always very intimately associated with galena is rather remarkable, and would seem to have some special significance.

#### Proustite from Cobalt, Ont., O'Brien Mine (?)

Crystals of proustite, supposedly from the O'Brien mine, have been described in detail by A. L. Parsons of the University of Toronto, and were analyzed by the writer. The following extracts from the article<sup>21</sup> referred to may be quoted:

The crystals for the most part are less than two millimetres in length and very few exceed a millimetre in diameter. They are light ruby-red in colour and exceedingly brilliant, and casual inspection suggested that they were proustite. As this mineral had not been described from the Cobalt region, it seemed desirable to confirm this supposition by chemical analysis and crystallographic measurement.

The material for analysis was obtained by floating the crystals from a large quantity of fine material which had broken away from the larger specimens. In this operation it was found that certain impurities accompanied the proustite, so that the final separation was made by means of a brush and lens. It was observed that many of the crystals still had a trace of what appeared to be smaltite attached to one end, but with the material at hand it did not appear feasible to remove the last trace of impurity.

It was also observed that in some instances the crystals were somewhat dark for proustite, and in most cases these were discarded, but the small amount of antimony found in the analysis would indicate that a little pyrargyrite is mingled with the proustite.

The analysis yielded the following results:

	Ag	As	S	Sb	Fe	Co (with trace of Ni)	Insol. in HNO <sub>3</sub>	Total
Per cent.	64.12	15.90	19.28	.08	.25	.12	.38	100.13

The percentages for silver, arsenic, sulphur and iron are the averages of two determinations for each. The determinations for antimony and insoluble were made only once, while the cobalt-nickel determination was obtained by combining the cobalt-nickel contents of two analyses.

<sup>21</sup> Proustite from Cobalt, Ont., by A. L. Parsons, in *Mineralogical Magazine*, Vol. XVII—No. 82—April, 1916.



If we assume that the iron is combined with sulphur in the form of pyrite and the cobalt with arsenic in the form of smaltite, the recalculation gives a nearly pure proustite with a small excess of arsenic as follows:

Element	Ag	As	S	Sb	Fe	Co
Per cent.	64.12	15.90	19.28	.08	.25	.12
Mol. Ratio	.5943	.2120	.6013	.0007	.0045	.0020
Pyrite	....	....	.0090	....	.0045	....
Smaltite	....	.0040	....	....	....	.0020
Proustite	.5922	.1974	.5922	....	....	....
Pyrrargyrite	.0021	....	.0021	.0007	....	....
Arsenic excess	....	.0106	Deficiency of S = .0020	....	....	....

Converting these ratios into percentages the following result is obtained:

	Proustite	Pyrrargyrite	Smaltite	Pyrite	Arsenic excess	Insol.	Total
Per cent.	97.69	.39	.42	.53	.79	.38	100.19

Less S added      .06

100.13

Owing to an error in calculating the molecular ratio for antimony in the original paper, the percentages of the mineral constituents given here differ slightly from those tabulated in the paper by Mr. Parsons.

### Polybasite Crystals, O'Brien Mine

Polybasite has long been supposed to be present in the Cobalt ores, but hitherto has not been positively identified by crystallographic measurements or chemical analysis.

Several years ago M. T. Culbert, of the O'Brien mine, presented to the museum of the University of Toronto, a specimen of argentite, showing a few minute crystals, which he believed to be polybasite, because of the triangular striations to be seen on some of the faces.

The writer examined this specimen with a view to extracting crystals for measurement. The minute, brilliant, thin tabular crystals, reaching a maximum diameter of perhaps two millimetres, are always firmly attached to the argentite, either by the large basal pinacoid or by one side, and had to be very carefully cut away. Finally, about ten crystals, together with some broken material, were

obtained. These were examined on the goniometer and all showed the same characteristic habit, but only one, which was about one millimetre in diameter, gave fairly good reflections. This one was measured as accurately as possible. The best readings for the side faces gave values of  $59^{\circ} 46'$ ,  $60^{\circ} 05'$  and  $59^{\circ} 10'$  for the outer angles between these faces, which agree closely with the values given by Penfield ( $60^{\circ} 02'$ ) and Goldschmidt ( $60^{\circ} 01'$ ) for the prism  $m : m$ . The base, as nearly as could be ascertained, was at  $90^{\circ}$  to the side faces. The vicinal faces, indicated in the drawing (Fig. 29), gave a continuous hazy band of light in which no definite points could be observed, from about  $16^{\circ}$  to about  $44^{\circ}$  from the base. This crystal had been attached by one side, and the lower half of the crystal showed exactly the same arrangement of vicinal faces as the upper, but because of the fragile nature of the crystal, no attempt was made to measure the vicinal faces on the lower half. The side faces which correspond to the prism  $m$  (110) are slightly concave, causing distortion of the signals, and a fracture parallel to the base divides the crystal

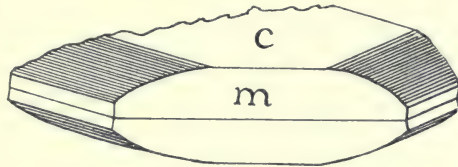


Fig. 29. Polybasite, O'Brien mine.

symmetrically into two equal parts, thus displaying perfect basal cleavage. This fracture was doubtless developed by cutting the argentite from around the crystal. Considered along with the re-entrant character of the prism faces, it suggests a twinning parallel to the base.

Polybasite has been considered by different authors to be either rhombic or monoclinic with twinning plane  $m$ , and probably also with a twinning like the micas, parallel to the base. Penfield, who is responsible for much of the later work on polybasite, considers it monoclinic, on both crystallographic and optical grounds.

Using the high power of the microscope, small, very thin particles of these crystals appear translucent and of a bright cherry red colour. This character distinguishes polybasite from the corresponding arsenic compound—pearceite, which is said to be "opaque even in the thinnest splinters."<sup>22</sup> The crystals are very brittle and rather soft.  $H = 2.5$  to  $3$ . Colour and streak black, lustre metallic, cleavage basal.

In order to further confirm the identification of these crystals as polybasite, the broken fragments obtained in trying to remove the crystals from the argentite were combined with those crystals which had proved useless for measurement and about 20 milligrams of powder was thus collected for analysis. Weighings were made only to the usual four places of decimals on a good balance and the analysis was necessarily at the same time both qualitative and quantitative, so that no great accuracy was attained. The results, however, confirm the decision, reached by means of crystallographic methods, that the mineral is polybasite.

<sup>22</sup> Hintze—Handbuch der Mineralogie.

## Analysis of polybasite crystals:

	Ag	Cu	Sb	S	Total
Per cent.	74 to 75	2	6+	12+	95
Theoretical Ag <sub>9</sub> SbS <sub>6</sub>	75.67	....	9.34	14.99	100.00

Reviewing all the evidence it is found that these crystals agree in form, physical properties, and chemical composition with the mineral polybasite (Ag,Cu)<sub>9</sub>SbS<sub>6</sub>, which is thus definitely established as a Cobalt mineral.

It was thought that the argentite to which the polybasite crystals were attached might show an admixture with massive polybasite, especially as certain spots showed an unusual brilliant, superficial tarnish like bornite. An analysis (page 11), however, yielded no more than traces of antimony and copper as impurities, so that there is no evidence to show that massive polybasite is present in quantity.

**Pink Carbonate**

An oxidized arsenide specimen from the O'Brien mine showed velvety coatings, one to two millimetres thick, consisting of very delicate needle-like crystal growths. On some parts of the specimen this coating was pure white, on others, a beautiful peach blossom pink. It was thought that the pink material might be roselite and it was accordingly analyzed.

Fe .....	2.33	per cent.	=	4.83	per cent.	Fe Co <sub>3</sub>
Co .....	0.80	"	=	1.35	"	Co Co <sub>3</sub>
Ca O .....	51.13	"	=	91.53	"	Ca Co <sub>3</sub>
Mg .....	.64	"	=	2.21	"	Mg Co <sub>3</sub>

Total..... 99.92

The material is evidently merely calcium carbonate with small amounts of iron and cobalt which give the colour. From optical tests and habit of growth it appears to be arragonite rather than calcite.

**Symplesite, Penn-Canadian Mine**

This material was examined because it was thought it might contain cobalt oxides such as heterogenite or heubachite which have been supposed to be present in some of the oxidized Cobalt ores.

The specimen represents weathered, oxidized ore such as was obtained at the surface in opening up the Cobalt veins. It consists of earthy masses of bluish black oxidized material, held together by spongy native silver or dyscrasite. In some spots a dirty pink colour indicates the presence of impure erythrite.

Under the microscope, the earthy material is seen to consist for the most part of grains which, when thin, are translucent to transparent, yellowish in colour and doubly refracting. Along with these are other opaque grains which are chiefly native silver or dyscrasite, and argentite.

*Chemical Properties*—The earthy part is readily soluble in five per cent. hydrochloric acid, and no unoxidized arsenides were detected in the residue. The insoluble part consists chiefly of native silver or dyscrasite, and argentite, with small grains of quartz. The argentite is not attacked by hydrochloric acid of this concentration, and no sulphur is found in the filtrate, showing that all the sulphur

obtained in the analysis is to be assigned to argentite. Qualitative tests show that the iron is practically all in the ferrous condition, though a very small amount of ferric iron was detected. On treating with strong hydrochloric acid no chlorine is evolved, showing that the cobalt and nickel are also in the lower state of oxidation. Water-soluble arsenic trioxide was not detected, neither by long standing (three weeks) with occasional shaking, at room temperature, nor by boiling for an hour or more.

*Preparation of Samples*—The material was gently rubbed in an agate mortar and two portions were separated for analysis.

1. Arsenate Part: The powder which passed a 250 mesh sieve. This was chiefly arsenates with particles of native silver or dyscrasite and argentite. The hope that the very fine sieve would eliminate most of the native silver proved to be unjustified because of the brittleness of the so-called silver which may be judged by the fact that the analysis indicates the presence of about 18 per cent. in this sample, all of which of course, had passed through the fine sieve along with the arsenates, after only moderate rubbing. The brittle character of the silver would lead one to suspect that it was really dyscrasite.

2. Silver Part: This constitutes the coarser, less brittle portions left behind on the sieve. These were freed from adhering arsenates by dilute hydrochloric acid, rinsed with ammonia to remove any silver chloride and then washed to get rid of small particles of argentite.

These two samples were analyzed with the following results:

Analysis of the arsenate part:

Element	Per cent.	Mol. Ratio	Argentite Ag <sub>2</sub> S	Native Silver, Dyscrasite and Anallgam	Symplesite Fe <sub>3</sub> As <sub>2</sub> O <sub>8</sub> ·8H <sub>2</sub> O	Erythrite Co <sub>3</sub> As <sub>2</sub> O <sub>8</sub> ·8H <sub>2</sub> O	Annabergite Ni <sub>3</sub> As <sub>2</sub> O <sub>8</sub> ·8H <sub>2</sub> O	Fe <sub>3</sub> As <sub>2</sub> O <sub>8</sub> ·8H <sub>2</sub> O R=Cu, Ca, Mg, Al
Ag	28.11	.2605	.1066	.1539	....	....	....	....
S	1.71	.0533	.0533	....	....	....	....	....
Sb	.79	.0066	....	.0066	....	....	....	....
Hg	.64	.0032	....	.0032	....	....	....	....
FeO	7.71	.1074	....	....	.1074	....	....	....
CoO	6.31	.0842	....	....	....	.0842	....	....
NiO	1.74	.0233	....	....	....	....	.0233	....
CuO	2.42	.0304	....	....	....	....	....	.0304
As <sub>2</sub> O <sub>3</sub>	24.60	.1070	....	....	.0358	.0281	.0078	.0301
Sb <sub>2</sub> O <sub>3</sub>	1.55	.0048	....	....	....	....	....	....
*H <sub>2</sub> O	13.64	.7577	....	....	.2864	.2245	.0622	.2512
CaO	2.58	.0460	....	....	....	....	....	.0460
MgO	.72	.0638	....	....	....	....	....	.0638
†CO <sub>2</sub>	(2.81)	.0638	....	....	....	....	....	....
‡CO <sub>2</sub>	.73	....	....	....	....	....	....	....
Al <sub>2</sub> O <sub>3</sub>	.30	....	....	....	....	....	....	....
Quartz	4.45	....	....	....	....	....	....	....
	(100.08)							
	98.00							

\* Direct determination of total water. H<sub>2</sub>O at 100°C not determined.

† Equivalent to CaO and MgO found.

‡ Actually found. One determination.

## Analysis of silver part:

	Ag	Hg	Sb	Argentite Insol.	S	Total
Per cent.	90.54	3.08	.79	5.50	trace	99.91

The arsenate sample could not be dried at 100° C. as it loses water, at first rapidly, then slowly, but continuously at that temperature. One gram heated for a half day at 100° C. lost 4.87 per cent.; one gram heated another half day, .22 per cent.; one gram heated another half day, .14 per cent. After allowing this dried sample to stand in the open for three days it had regained its original weight. In order to secure uniform sampling, the material, without previous heating, was all weighed out at one time into gram quantities and kept in clamped watch-glasses till required.

The duplicate analysis of the arsenate part gave closely concordant results, but there is some uncertainty as to the way in which some of the actual analytical results should be recalculated, and certain assumptions have been made which may not be altogether justifiable. For example, the total antimony found has been divided into two portions as Sb, and Sb<sub>2</sub>O<sub>5</sub>. The amount of antimony found in the silver part has been tabulated as such in the arsenate part, assuming it to be in the form of dyscrasite, but it is not improbable that the silver which was mixed with the arsenates was richer in antimony than the coarser, more ductile sample analyzed as part 2, and, therefore, a larger proportion of the total antimony should really be deducted to make dyscrasite. An attempt was made to analyze the silver mixed with the arsenates by extracting the arsenates with dilute hydrochloric acid, but the silver was in such a finely divided condition that even the dilute acid changed it almost completely to the chloride while mercury and antimony passed into solution. A titration with permanganate of a sulphuric acid solution of the arsenates made in an atmosphere of carbon dioxide gave almost exactly the same results for iron as the gravimetric determination. Carbon dioxide is believed to be present in much smaller amount than would be required to combine with the CaO and MgO found. The single carbon dioxide determination on about 2 grams of material could not be expected to give results of great accuracy, but the quantity found confirms the suspicion that the lime and magnesia are not present entirely as carbonates. When the material is treated in a small test-tube with strong hydrochloric acid, a slight evolution of gas can be detected with a hand lens, but would not be noticed by the naked eye. In fact, the presence of carbonates was not suspected until analysis revealed calcium and magnesium in the mixture. Calcium and magnesium are often found in considerable quantity in the arsenates of this series and no doubt in this case, also, are chiefly in the form of arsenates.

*Mineral Constituents.*—From the foregoing chemical data the mineral composition of the mixture has been calculated as indicated in the table. All the sulphur is combined with silver to form argentite. Mercury and the amount of antimony found in the silver part (2) are associated with the rest of the silver as dyscrasite and amalgam. It may be noted that the amount of mercury relative to silver is

approximately the same in both analyses, but is a little higher in the more brittle silver of the arsenate part.

In arsenate part Ag: Hg = 16.61: 64

In silver part Ag: Hg = 90.54: 3.08

Since the iron is in the ferrous condition it has been calculated as symplecite, the iron arsenate corresponding to erythrite and annabergite. Symplecite has not been recognized hitherto in Cobalt ores, though it might be expected to occur. Cobaltous and nickelous oxides are calculated to erythrite and annabergite respectively.

So far there can be little doubt that the calculation represents the true mineral composition. There are, however, many arsenates of copper, while calcium and magnesium arsenates are known, and these elements may also replace cobalt or nickel in erythrite and annabergite, according to analyses recorded by Dana. If a compound  $R_3As_2O_8 \cdot 8 H_2O$  ( $R = Ca, Mg, Cu, Al$ ) analogous to erythrite be calculated for the lime, magnesia and copper oxide found then small amounts of arsenic and antimony pentoxides remain uncombined and a little more water than was found in the analysis is required. Certain of the copper, calcium, and magnesium arsenates, however, contain less water and more arsenic than the assumed compound and some of these may be present. The excess of arsenic would also be explained if a small amount of native arsenic were present. If so, it must be in a very finely divided condition and would be difficult to detect.

The percentages of the different minerals so far as they may be definitely calculated are given below:

	Argentite	Native Silver with Sb and Hg	Symplecite	Erythrite	Annabergite	Arsenates of Cu, Ca, Mg, etc.	Quartz	Total
Per cent.	13.21	18.04	21.09	20.60	4.65	about 18.00	4.44	100.03

### Earthy Scorodite and Erythrite, Temiskaming and Hudson Bay Mine

The erythrite of Cobalt occurs usually as earthy incrustations on oxidized smaltite, crystallized material being rather uncommon. A sample of the earthy material of yellowish pink colour from the Temiskaming and Hudson Bay mine was examined for free arsenic trioxide and incidentally was found to contain a relatively large amount of ferric iron. This appeared to indicate the presence of scorodite, so the sample was analyzed with results as below:

	Fe <sub>2</sub> O <sub>3</sub>	CoO	NiO	As <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O (total)	CuO	As <sub>2</sub> O <sub>3</sub> (Sol. in H <sub>2</sub> O)	Insol.	CaO	Σ	Total
Per cent.	8.73	21.43	3.95	38.45	24.22	small am't	trace	2.90	trace	trace	99.68
Atomic Ratio	.0547	.2859	.0529	.1673	1.346	....	....	....	....	....	....
Scorodite Fe <sub>2</sub> O <sub>3</sub> .As <sub>2</sub> O <sub>3</sub> .H <sub>2</sub> O	.0547	....	....	.0547	.2188	....	....	....	....	....	....
Erythrite Co <sub>3</sub> As <sub>2</sub> O <sub>8</sub> +8H <sub>2</sub> O	....	.2859	....	.0953	.7624	....	....	....	....	....	....
Annabergite Ni <sub>3</sub> As <sub>2</sub> O <sub>8</sub> +8H <sub>2</sub> O	....	....	.0529	.0176	.1408	....	....	....	....	....	....
Excess	....	....	....	.0003	.224	....	....	....	....	....	....

On gently rubbing the material to a powder, the yellowish tint became more prominent and when some of the larger lumps were broken open, yellow spots were visible which were found to be chiefly ferric arsenate. The copper appears to be associated with the scorodite. Only a trace of water-soluble arsenic trioxide was obtained after treating the material with water for three weeks at room temperature. The total water obtained in the analysis probably includes more or less merely hygroscopic water, and perhaps, may also represent a slight loss of arsenic acid. The arsenic determinations were made on separate portions. Qualitative tests show that the iron is all in the ferric condition. The analytical results thus indicate that an important amount of scorodite is present in this earthy arsenate material.

#### On Isomorphism as Displayed by Certain Minerals from Cobalt

Analyses of even the most carefully selected samples of apparently pure, simple minerals from Cobalt such as, say, niccolite or smaltite, have, in the writer's experience, invariably revealed the presence of so-called isomorphous replacing elements, e.g., Fe Co, Sb and S in niccolite, Ni, Fe and S in smaltite. Such an experience is, moreover, not at all unusual, as witness the numerous similar analyses in any handbook on mineralogy. It has been usual with most mineralogists to regard such foreign elements as replacing in a molecular way a corresponding amount of the elements essential to the pure mineral. The writer, in examining polished surfaces of such minerals after etching with acid, has always found inclusions of one or

more different minerals present which might easily account for the foreign elements found by analysis. As has been seen in the case of cobaltite and smaltite, even the most perfect crystals may contain considerable amounts of foreign minerals either as inclusions or intergrowths. Such inclusions are very likely to be a mineral or minerals similar in crystal symmetry and analogous in chemical composition to the including mineral; e.g., the inclusions of niccolite in breithauptite (Fig. 8), or the smaltite-chloanthite intergrowth (Fig. 17). This is not always the case, however, examples of the latter type of intergrowth are furnished by inclusions of cobaltite (cubic) in niccolite (hexagonal), Fig. 13, and rammelsbergite (rhombic) in niccolite, Fig. 26. The former type of associations appears to be mixtures or intergrowths of more or less related, or isomorphous individual minerals, rather than homogeneous molecular mixtures.

Most of our knowledge of isomorphism rests on the data of chemical laboratory experiments. Nernst<sup>23</sup> refers to isomorphous mixing as "the capacity of two crystallized substances for uniting to form a homogeneous mixed crystal." Retgers<sup>24</sup> speaks of "the property of forming solid molecular mixtures." The chemist takes special precautions in order to obtain homogeneous mixed crystals. Retgers recommends in making mixed crystals, that "in order to obtain a product as homogeneous as possible, it is best to use a large quantity of solution and to study only the crystals which separate first."

In nature, however, these ideal conditions are probably seldom realized, and in the case of the arsenides and sulpharsenides of Cobalt, at least, the result is oftener a very intimate mixture or intergrowth of the two isomorphous substances than a true homogeneous molecular mixture, even when good crystals are formed. The etching methods described in the introduction enable us to distinguish very definitely the different components of such a mixture. The separation experiments performed on certain of these mixtures, e.g., niccolite-breithauptite, smaltite-chloanthite, seem to show that the individual components may be precipitated side by side as minute particles in extremely intimate microscopic mixtures or intergrowths and still retain their chemical identity and purity. There is this difficulty, however, with such etching separations, that only the residue may be expected to be pure and homogeneous, and if such a pure residue is obtained, it does not prove that some of the material which dissolved was not a homogeneous molecular mixture. It seems certain, however, that in most of the mixtures examined by the author, the amount of material which may represent true isomorphous molecular mixtures must be small compared to the amount which exists as pure chemical individuals.

Whether special conditions of precipitation were responsible for this character of the Cobalt minerals or whether it is a general characteristic of the arsenide and sulpharsenide groups of minerals, is a problem for the future. Baumhauer<sup>25</sup> and Vollhard<sup>26</sup> were the first to show that crystals of smaltite or chloanthite (from European localities) were really intergrowths, the different parts of which varied in composition. The writer suspects that such intergrowths are general among the minerals of these groups and that true molecular isomorphous replacements or mixed crystals are correspondingly rare.

<sup>23</sup> W. Nernst—Theoretical Chemistry.

<sup>24</sup> *Idem*, page 109.

<sup>25</sup> *Loc. Cit.*



It appears to the writer that such structures as the smaltite-chloanthite and the niccolite-breithauptite intergrowths afford some evidence of the degree of isomorphism exhibited by the minerals concerned, granting, of course, that these structures have resulted from practically simultaneous precipitation of the constituents from the same mother solution. The term isomorphism, of course, implies more or less complete identity of crystal symmetry. In this sense, these minerals are isomorphous. The property of mutual overgrowth is possessed by substances which have not the slightest chemical or crystallographic similarity and has accordingly been rejected by Retgers as conclusive evidence of isomorphism. Accepting complete miscibility or the property of forming homogeneous mixed crystals in all proportions as the most decisive criterion of pure isomorphism, as advocated by Retgers, we are led to the conclusion that the minerals with which we have been dealing, such as niccolite-breithauptite, smaltite-chloanthite, probably do not form molecular mixtures in every proportion and, therefore, do not exhibit the highest degree of isomorphism, in spite of their similar crystal form and analogous chemical composition. The same holds true for the cobaltite crystals with their gersdorffite (?) inclusions.

Following the classification of miscibility according to Retgers, these minerals appear to display limited miscibility of a sort.

#### Order of Deposition of Cobalt Minerals

The writer has not been concerned primarily with the study of the paragenesis of Cobalt minerals, but the apparent order of formation has been indicated for the associations which have come under his observation. For a complete study of this question very complete data would be necessary and final conclusions are probably



Fig. 30. Diagram of portion of vein from Silver Bar mine, natural size, showing order of deposition. The shaded part represents smaltite-chloanthite intergrowth with chloanthite in the centre of dendritic growths. The hatched part is later niccolite and the white is calcite.

not justified by a microscopic study of isolated specimens alone. As the writer's conclusions, however, agree in the main with those of W. G. Miller and C. W. Knight, they are here summarized.

From the numerous extremely intimate intergrowths which have been observed among the Cobalt minerals, e.g., smaltite-chloanthite, niccolite-breithauptite, etc., it is believed that certain of these minerals were precipitated in greater or less

quantity at the same time. The structures observed appear to indicate that the mineralizing solutions at first were relatively very rich in arsenic and during this time intergrowths of diarsenides-smaltite and chloanthite—were chiefly precipitated. The arsenic content of the solutions gradually diminished and monarsenides-nicolite and breithauptite—were for a time predominately deposited. The arsenic continued to decrease in amount and sulphur became prominent, so that sulpharsenides, such as cobaltite and arsenopyrite, were deposited. Finally, the arsenic in solution was reduced to a very small quantity, and calcite was deposited. A period of fracturing ensued and the solution which may now have been of either a sulphate or carbonate character circulated through the fractured veins. From this solution native silver and argentite were precipitated by the action of arsenides and calcite, resulting in such silver replacement structures as we have seen (Fig. 30).

It is believed that the process of deposition of the various arsenides and sulpharsenides was more or less continuous, and that, though a period of maximum deposition for any one of these minerals may be distinguished, there is, nevertheless, no sharp dividing line between the different periods.

The apparent order of deposition from the writer's observations may be indicated in tabular form as follows:

I. Arsenides and Sulpharsenides	{	1. Diarsenides	{	Ni As <sub>2</sub> Co As <sub>2</sub>
		2. Monarsenides	{	NiSb NiAs
		3. Sulpharsenides	{	Co As S Fe As S

II. Calcite, followed by fracturing.

III. Native silver and argentite, native bismuth, sulphides and sulpho-salts.

IV. Decomposition products—arsenates of cobalt, nickel, iron, copper, and calcium.

In conclusion, the writer wishes to thank T. L. Walker, Professor of Mineralogy at the University of Toronto, not only for much kindly advice and encouragement, but also for the original suggestion which initiated this work.









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